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Nottingham Fuel
& Energy Centre

Coal science: a melting pot for discovering and developing new analytical approaches

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Over 25 years association with the Div. Of fuel Chem.

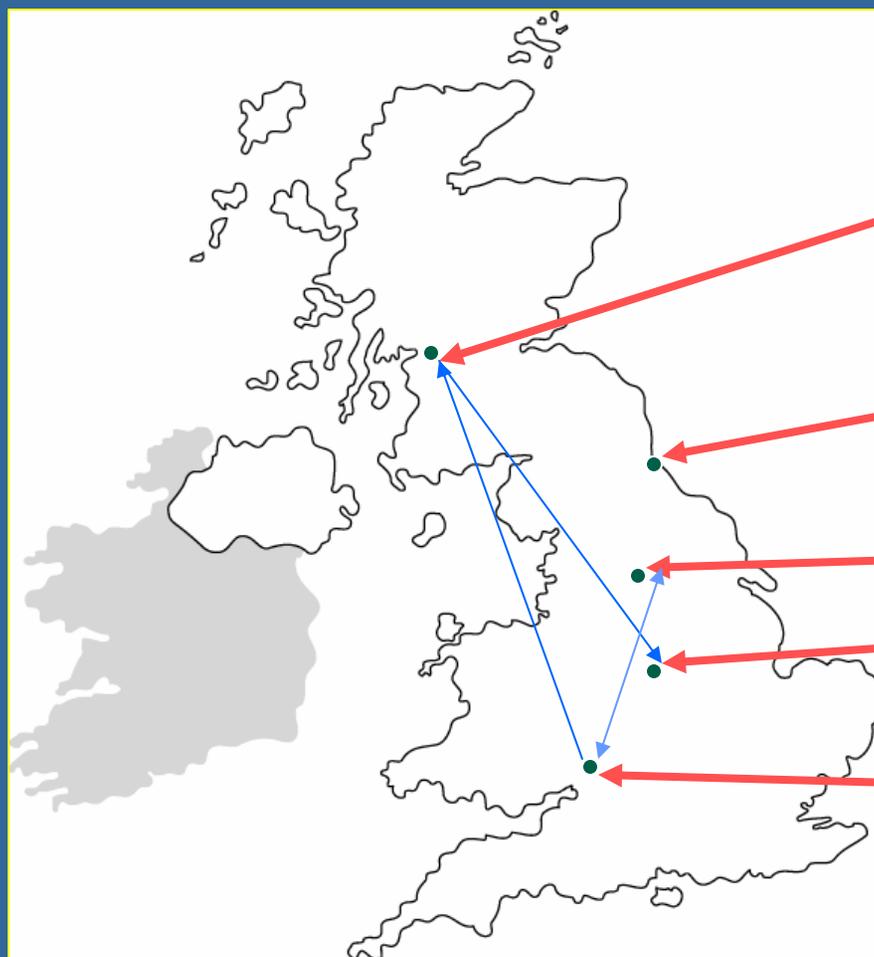
“The challenge of elucidating the highly heterogeneous structure of coal and its impact on thermal conversion behaviour has resulted in coal science being at the forefront for discovering and developing new analytical approaches for insoluble organic matter”

True?

Scope of presentation

- Evidence from solid state NMR and high pressure pyrolysis (hydropyrolysis) as examples that had a significant impact in other fields, notably polymer degradation and organic geochemistry.
- There are other such examples that could be used, since the renewed interest in coal research during the 1970s, e.g. RuO_4 oxidation (Stock), XPS (Gorbaty et al.).
- The process has worked in reverse, and, as an example, compound specific stable isotope analysis, developed primarily in geochemistry, will be described for differentiating sources of coal-derived pollutants - PAHs.
- Key challenges for the future development of clean coal technology will be summarised.
- *First – how did I get here?*

A journey in coal science



Univ. of Strathclyde,
Glasgow (1987-2000)

Sunderland (1953-71)

Durham coalfield

Univ. of Leeds
(Ph.D, 1977-81)

Univ. of Nottingham,
2000-present

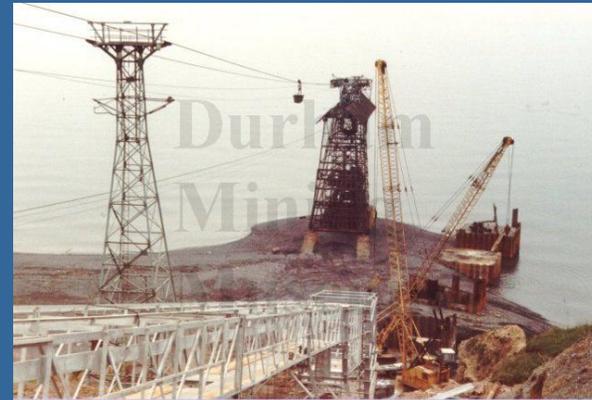
Coal Research
Establishment,
Stoke Orchard,
1974-87

The North East Coalfield in the 1960s and 70s



Durham Mining Museum

Hawthorn Mine and Coking Plant



Durham Mining Museum

© W. Stoker

Easington Colliery



Wearmouth Colliery



"Get Carter" 1972, Horden "Beach"

Coal Research Establishment, Stoke Orchard (1974-1987)



- How I got a job - as the supposed son of a militant union leader!
- Oil price rise – coal liquefaction would meet future needs.
- Bill Ladner, Derek Williams, Geoff Kimber, John Newman

Low-severity coal liquefaction products provided detailed insights into coal structure

- NCB developed supercritical gas extraction and two-stage hydrogen-donor solvent liquefaction processes, the latter operated at 2 t/d at Point of Ayr.

Structural analysis of supercritical-gas extracts of coals

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†National Coal Board, Coal Research Establishment, Stoke Orchard, Cheltenham, Glos. GL52 4RZ, UK

(Received 16 September 1978)

The chemical structure of two extracts prepared by supercritical extraction of low-rank coals with toluene, with and without hydrogen, have been determined using solvent and chromatographic fractionation followed by ultimate analysis, ^1H nuclear magnetic resonance (n.m.r.) spectroscopy, molecular weight and OH measurements. ^{13}C n.m.r. and i.r. spectroscopy have been used to obtain confirmatory evidence. The extract obtained in the absence of hydrogen, which amounted to 27% of the coal, was found to contain aromatic structures linked by ring-joining methylene or heterocyclic groups. The hydrogen-assisted extract (47.5 wt % coal) was more condensed and contained more smaller molecules, apparently as a result of the cleavage of heterocyclic groups in the coal. It also incorporated more hydroaromatic substituents. ^{13}C n.m.r. showed that virtually all the non-phenolic oxygen was present as aromatic ether.

Fuel, 1979, 58, 413-422 and Ph.D thesis

High vol. bit coals contain:

- Small aromatic nuclei.
- Little naphthenic/hydroaromatic structure
- Short alkyl chains.

Presented at 1980 ACS meeting in Las Vegas.

My “Scientific” Family Tree

Prof. Keith Bartle,
Univ. of Leeds

Dr. Bill Ladner,
Coal Research Establishment

Colin Snape

Gordon Love,
Ian Murray, Chris
Russell, Will
Meredith

Hydropyrolysis
– biomarkers in oil
exploration

Rob Law, John Andresen
Mercedes Maroto-Valer
Caroline Dick, Shona Martin

Solid state NMR

- Coal carbonisation /oil
conversion
- Fire retardants/polymers

Carole McRae,
Cheng-Gong Sun

Sourcing coal-
derived PAHs in the
environment

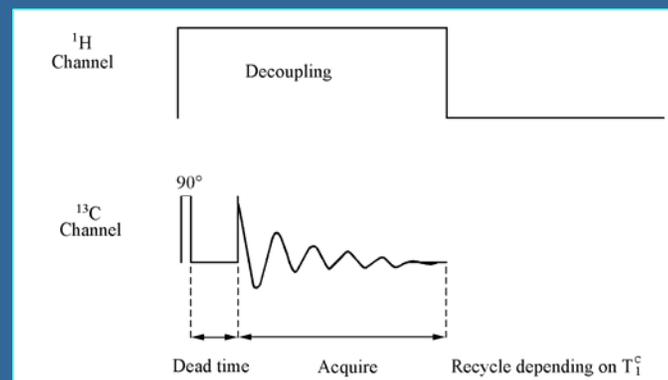
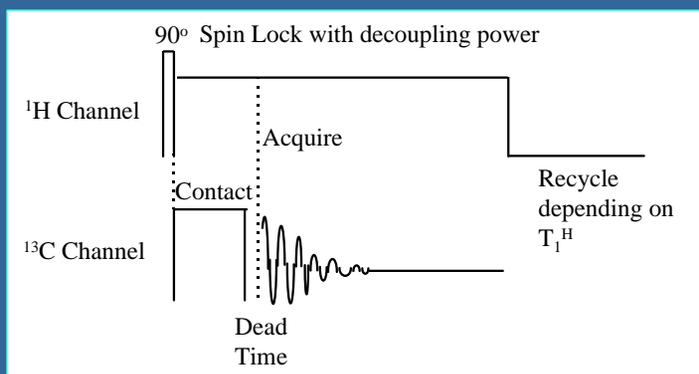
Quantitative solid state ^{13}C NMR

– *carbon skeletal parameters to model thermal conversion*

■ Easy to do badly, but painstaking to do well!

Cross-polarisation. Fast, but inevitably non-quantitative – not all C observed, discriminates against aromatic C.

Single pulse excitation, slow and less sensitive, but quantitative – all the C observed.



■ Proven for coal then applied to all insoluble organic matter

– polymers, petroleum source rocks, catalytic cokes (FCC), semi-cokes.

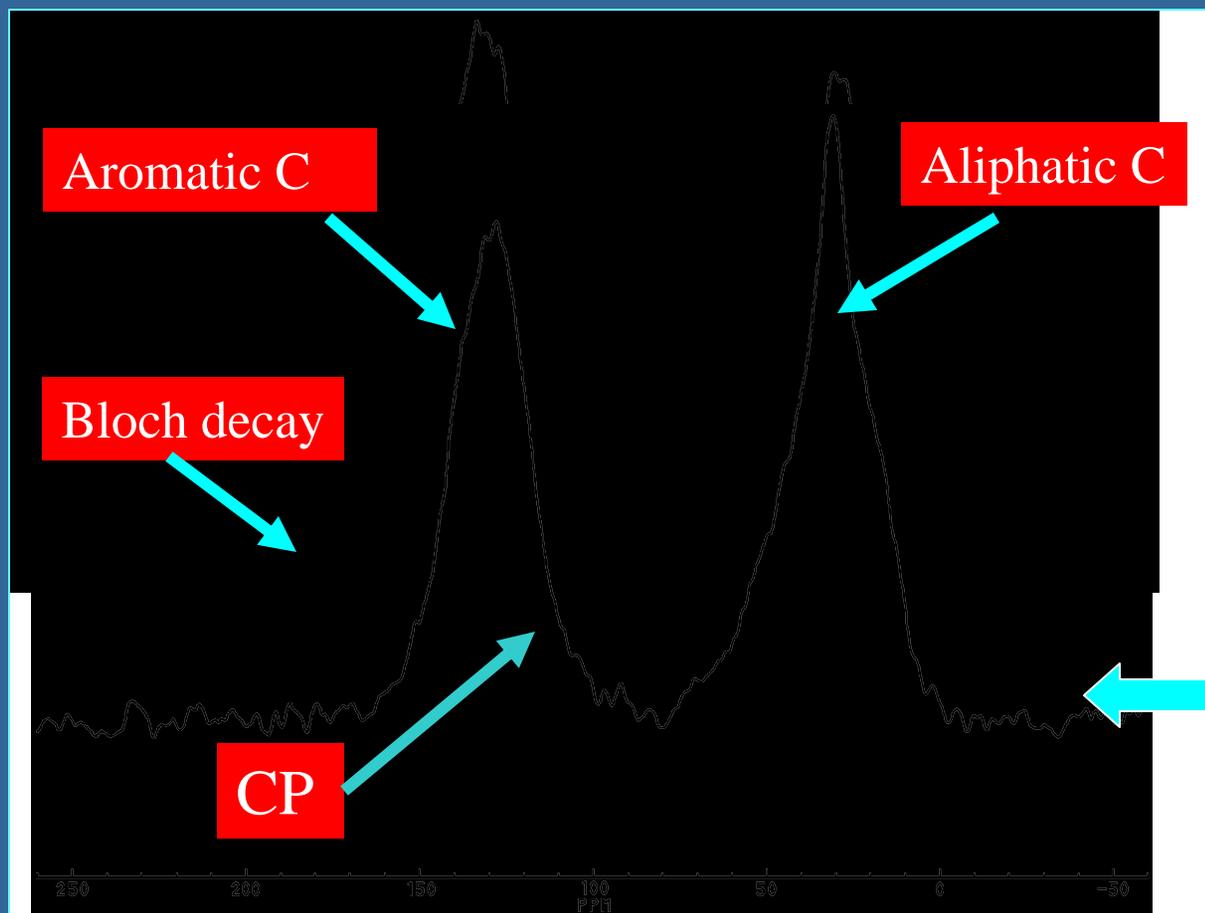
■ SPE - higher aromaticities and more non-protonated aromatic C.

K.J. Packer, R.K. Harris, A.M. Kenwright and C.E. Snape, *Fuel*, 1983, **62**, 999-1002.

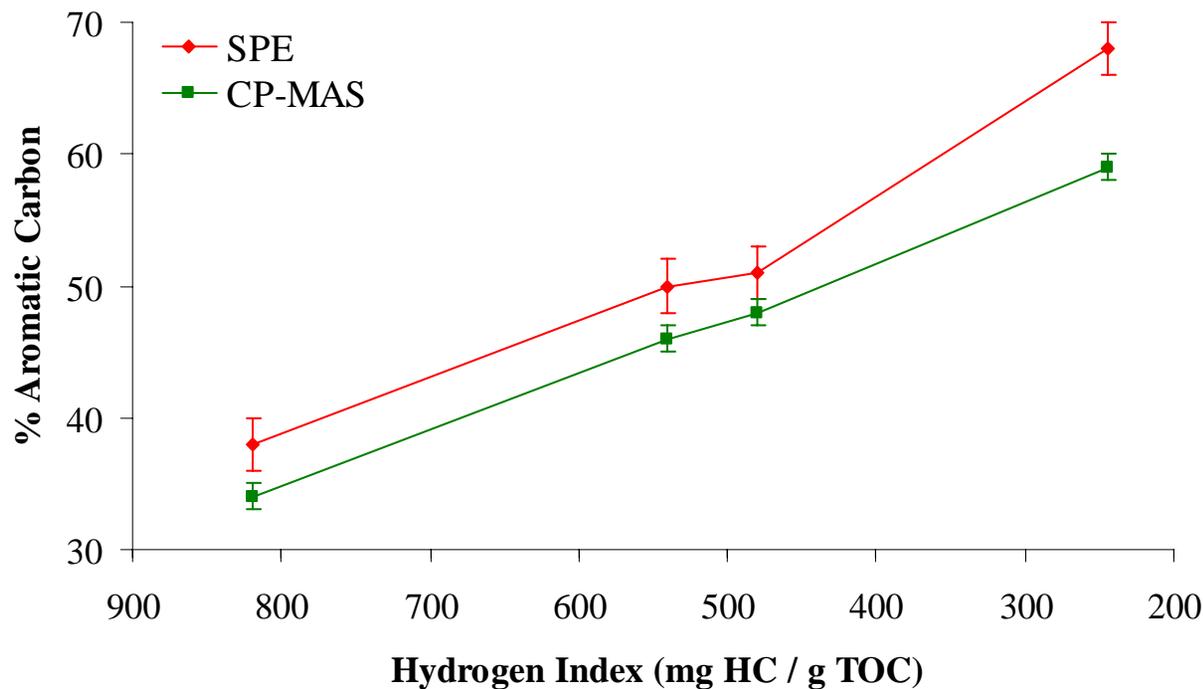
C.E. Snape, D.E. Axelson, R.E. Botto, J.J. Delpuech, P. Tekely, B.C. Gerstein, M. Pruski, G.E. Maciel and M.A. Wilson, *Fuel*, 1989, **68**, 547-560.

J. Franz, R. Garcia, G.D. Love, J. Linehan and C.E. Snape, *Energy & Fuels*, 1992, **6**, 598-602.

Solid state ^{13}C NMR Spectra of an petroleum source rock (type 1 kerogen) matured by hydrous pyrolysis



Aromaticity comparison of SPE and CP solid state ^{13}C NMR for type II petroleum source rock maturity suite



Difference between CP and SPE greatest for most mature kerogen.

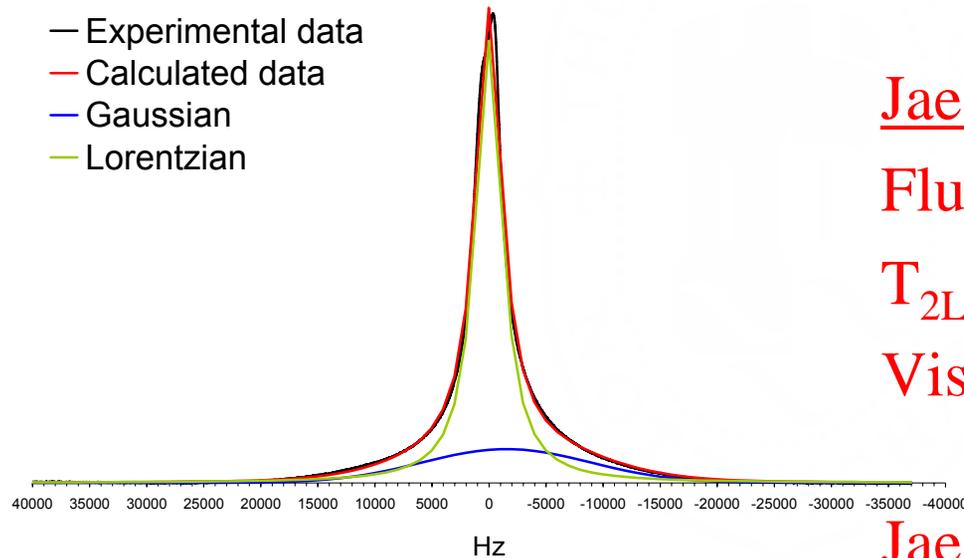
Relatively small differences of 5-10% in aromaticity have major influence on overall balances of aromaticity and carbon skeletal parameters to model oil generation.

Broadline ^1H NMR

Quantify fluidity and then you understand carbonisation

- In-situ broadline ^1H NMR has proved highly successful for investigating molecular motion in coals and pitches during carbonisation – pioneering work of Lynch and Sanada.
- Usually there are two contributions to free induction decays of coals that arise from mobile (faster relaxing) and rigid (slower relaxing) components that display Lorentzian and Gaussian decays, respectively.
- Coal gives rise to a substantial inert component that does not soften and produces a broad Gaussian peak with a narrower Lorentzian peak from mobile material superimposed.

Deconvoluted ^1H NMR spectra (at maximum fluidity – 450°C)

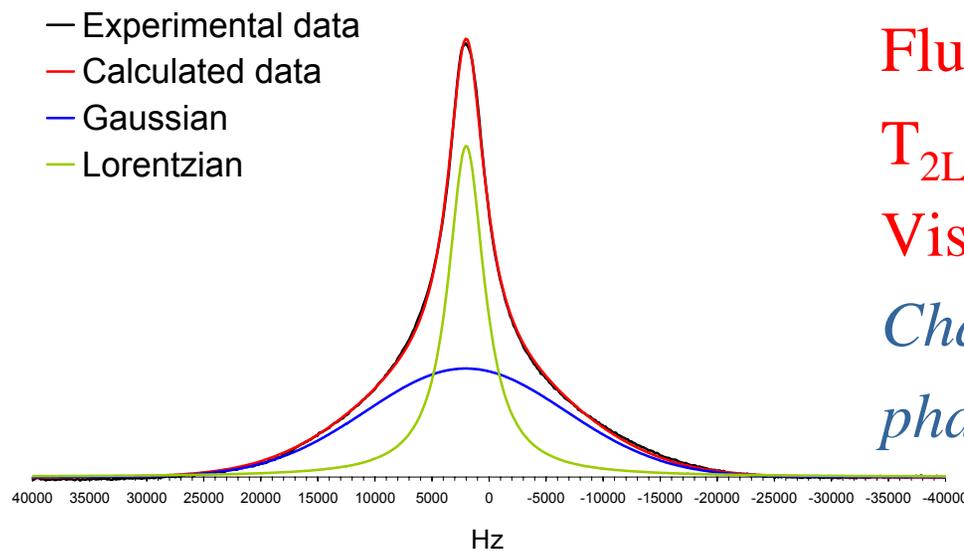


Jaeger coal

Fluid H = 73 %

$T_{2L} = 103 \mu\text{s}$

Viscosity = $6.2 \times 10^3 \text{ Pa}\cdot\text{s}$



Jaeger (80%) + Charcoal (20%)

Fluid H = 51 %

$T_{2L} = 91 \mu\text{s}$

Viscosity = $8.8 \times 10^4 \text{ Pa}\cdot\text{s}$

Charcoal addition reduces fluid phase and shortens T_{2L}

Some well-known (qualitative) facts about carbonisation

Quantification by in-situ ^1H NMR

- Mild air oxidation is detrimental
- Fluidity generation is reversible with rapid heating.
- Pitch additives enhance fluidity.
- Semi-fusinite is reactive, contributes to fluidity.

Other debatable points answered

- Influence of particle size? Reduces T_2 not % fluid H.
- How much fluid phase is derived from pyridine extractables? *ca.* 50%

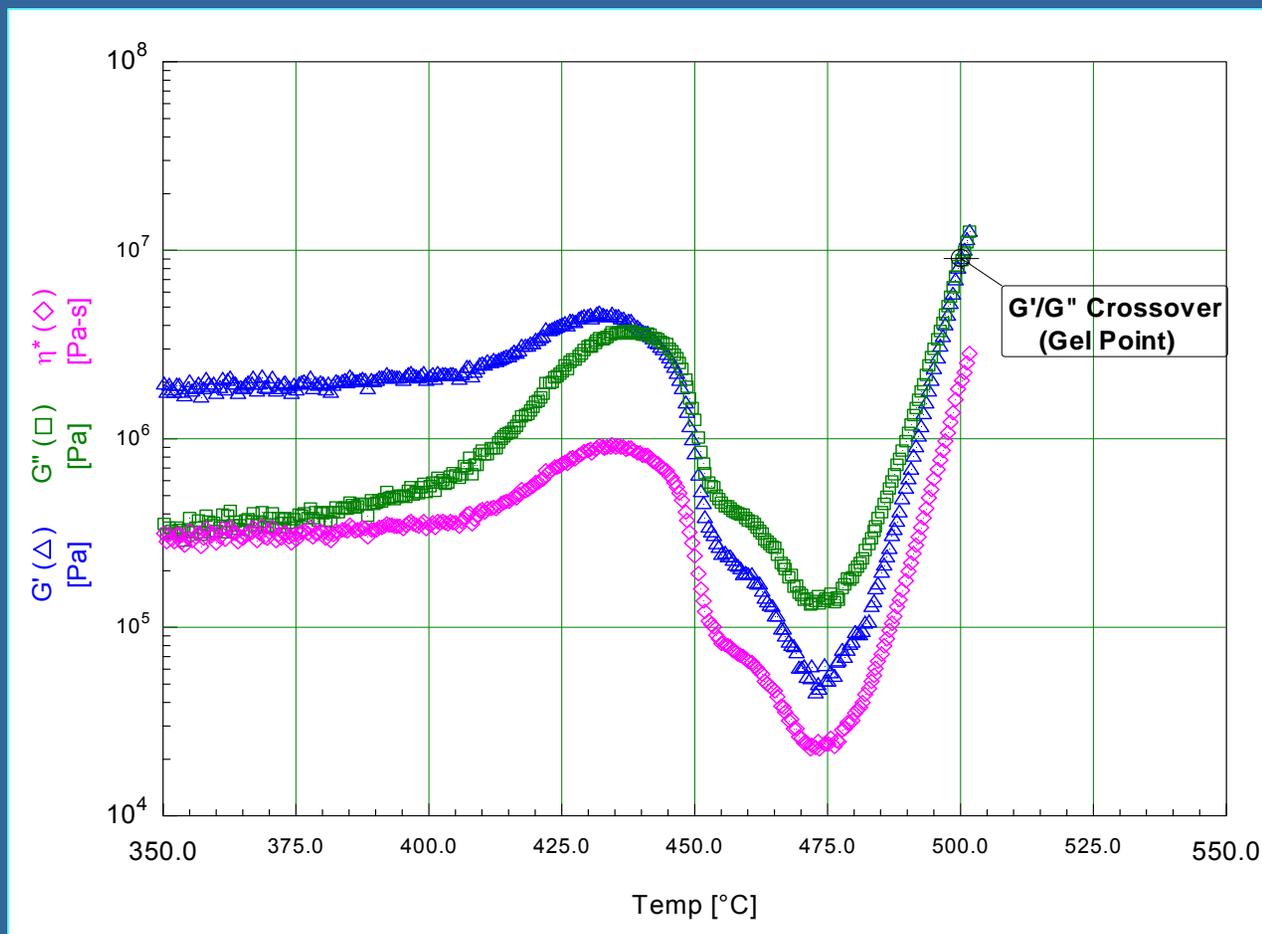
M.M. Maroto-Valer, J.M. Andrésen and C.E. Snape, In-situ ^1H NMR investigation of particle size, mild oxidation and heating regime effects on fluidity development during coal carbonisation, Energy & Fuels, 1997, 11, 236-244.

M.M. Maroto-Valer, D.N. Taulbee, J.M. Andrésen, J.C. Hower and C.E. Snape, The role of semifusinite in plasticity development for a coking coal, Energy & Fuels, 1998, 12, 1040-1046.

Information from rheometry

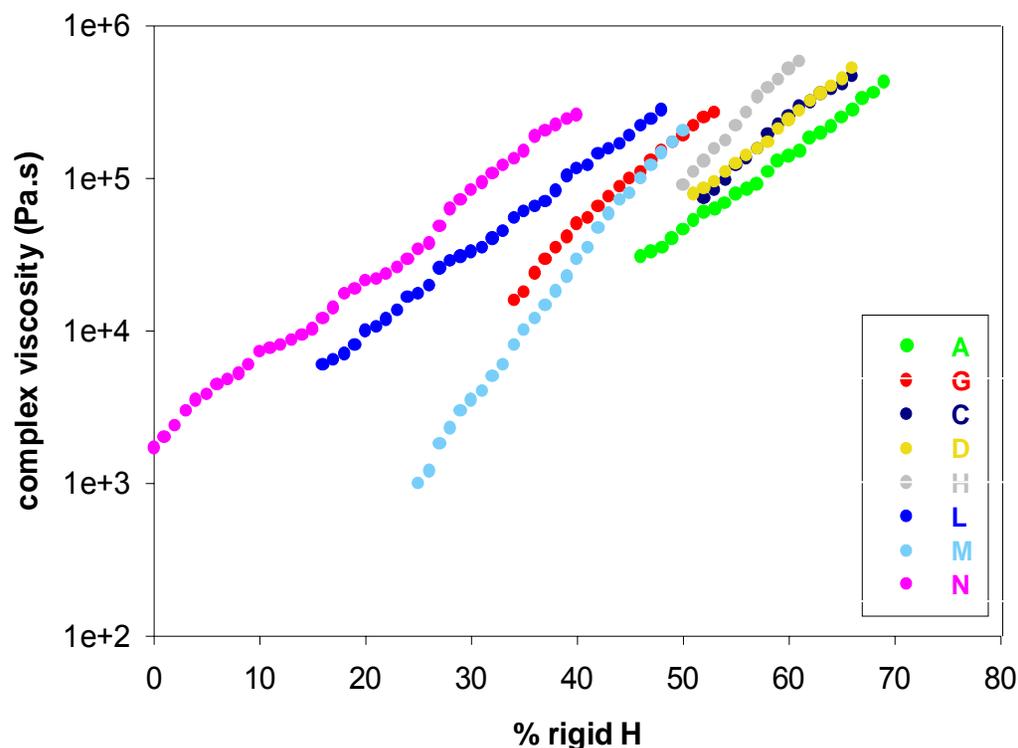
— *sol to gel transformation during resolidification*

Small amplitude oscillatory shear measurements
sample between two parallel plates



- G' is proportional to elastic energy stored and recovered.
- G'' is proportional to energy dissipated in flow.
- For elastic materials, $G''/G' = 0$
- For viscous materials, G''/G' is large.

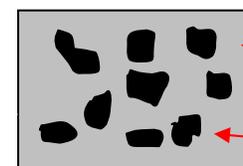
Combining rheometry with ^1H NMR (resolidification)



cross-link density
high enough for
solid-like behaviour
(gel point)



**resolidified
material** (higher
intrinsic viscosity)

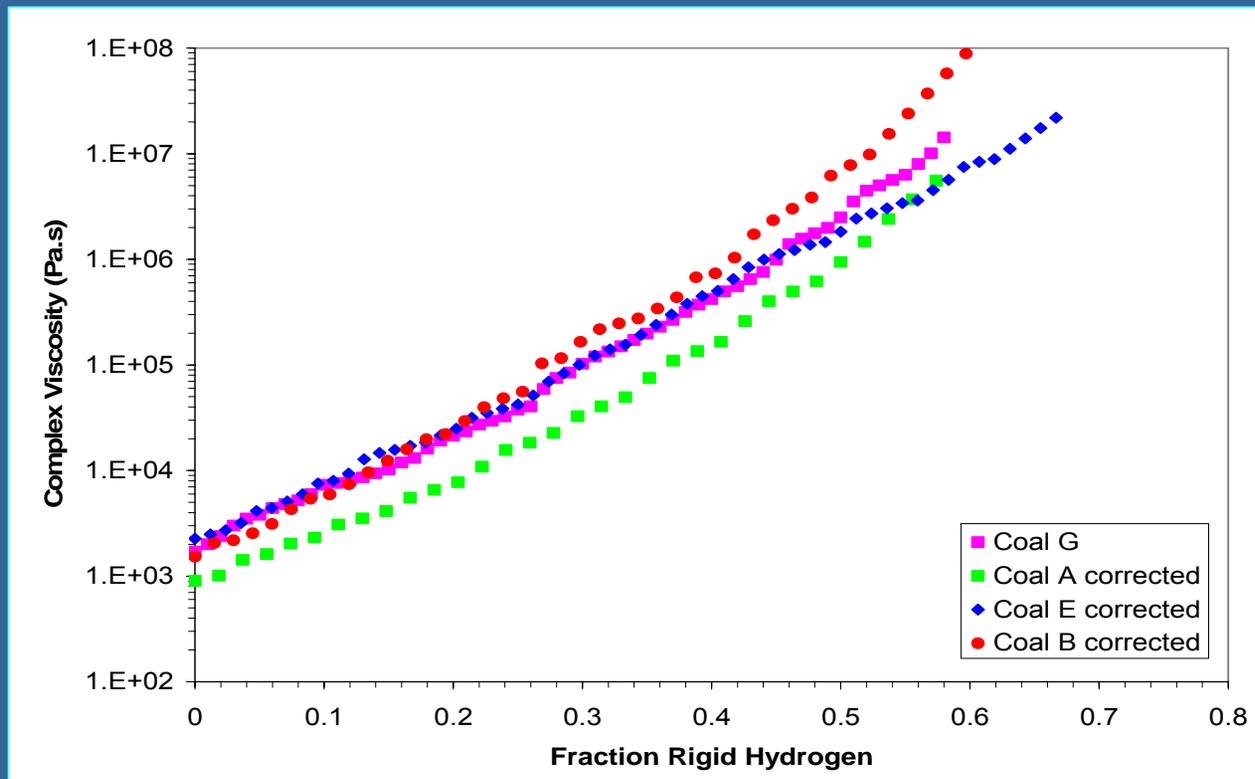


**liquid
material**
inert solid (low
intrinsic viscosity)

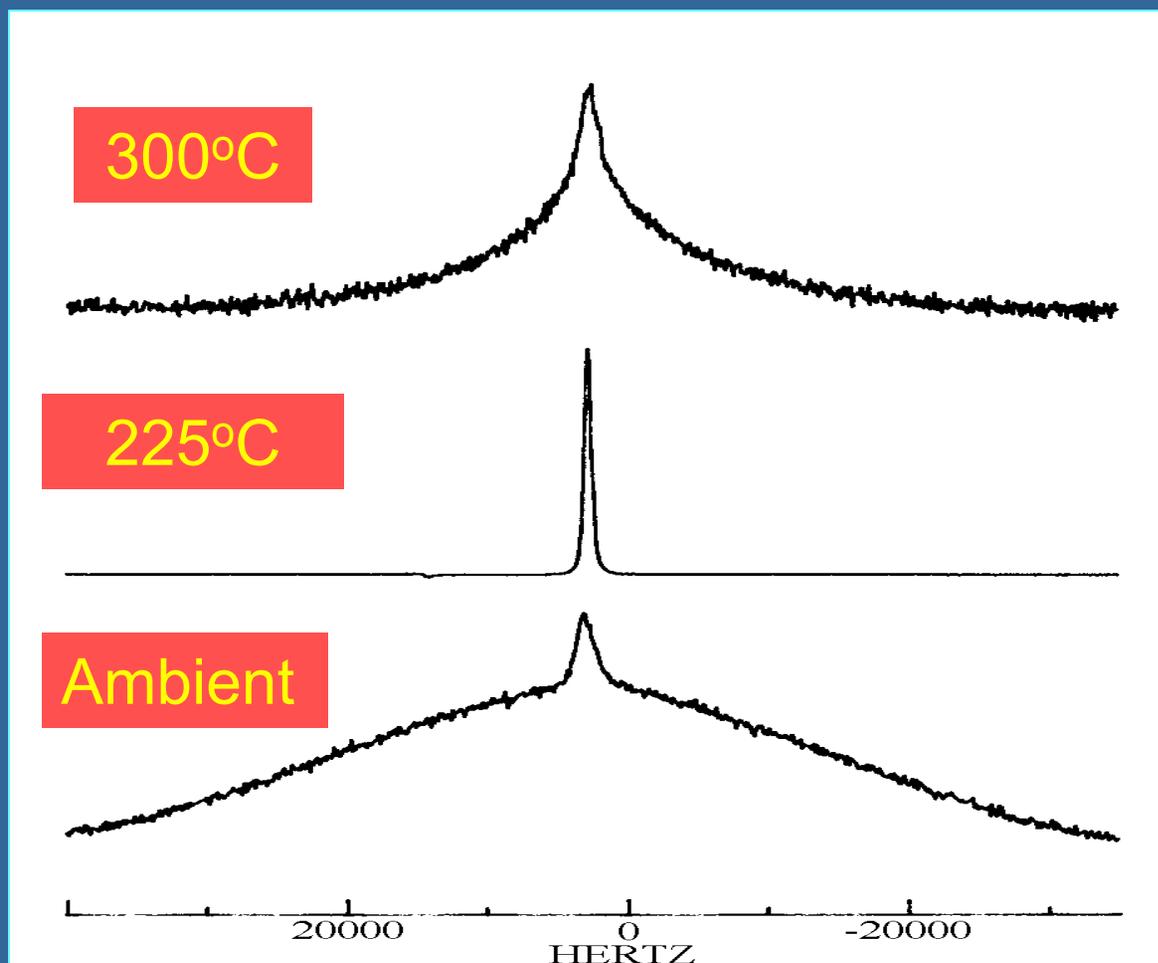
- Exponential relationship occurs for all the coals studied.
- Position of curve (horizontal shift) depends largely on how much rigid H is present as inert solid, and how much is resolidified material (have different intrinsic viscosities).

Combining rheometry with ^1H NMR (resolidification)

- Common exponential relationship exists once correction made only to include newly formed solidified material.
- Gel point is common and occurs when the proportion of rigid H is 60%.



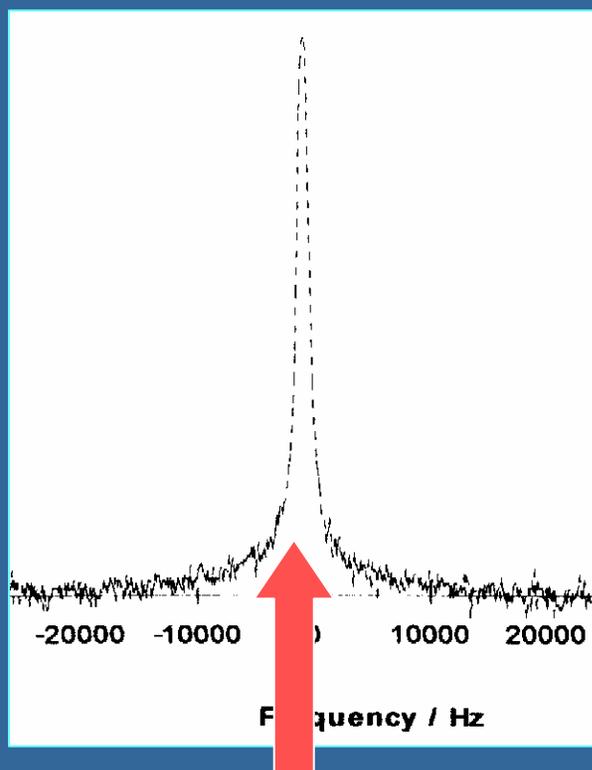
Broadline ^1H NMR spectra of Polyvinylchloride - PVC ($-\text{CH}_2\text{CHCl}-$)



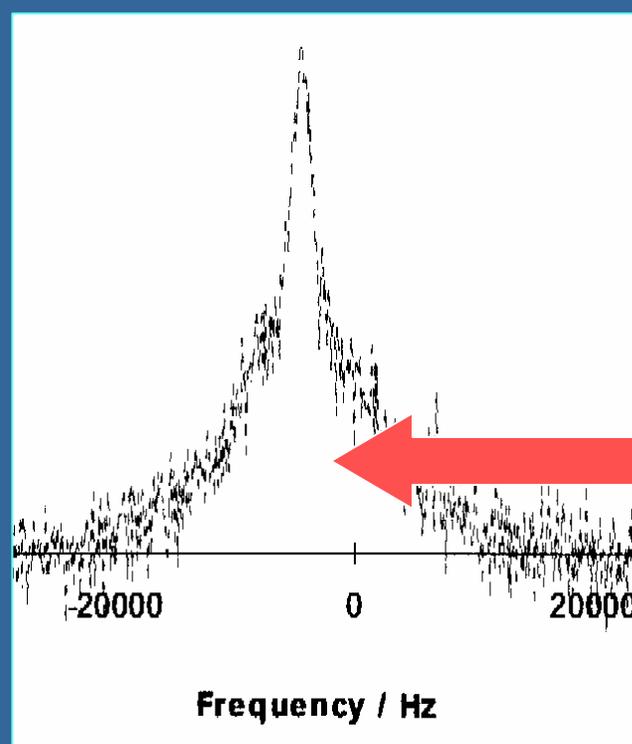
PVC loses HCl and forms rigid char at low temperature giving inherent fire retardancy.

Condensed phase action of a fire retardant (melamine) for a flexible polyurethane foam

^1H NMR spectra at 450°C



Highly fluid, no retardant



Retardant promotes char formation

C.M. Dick, E. Dominguez-Rosado, B. Eling, J.J. Liggat, C.J. Lindsay, S.C. Martin, M.H. Mohammed, G. Seeley and C.E. Snape, *Polymer*, 2001, 42, 913-923.

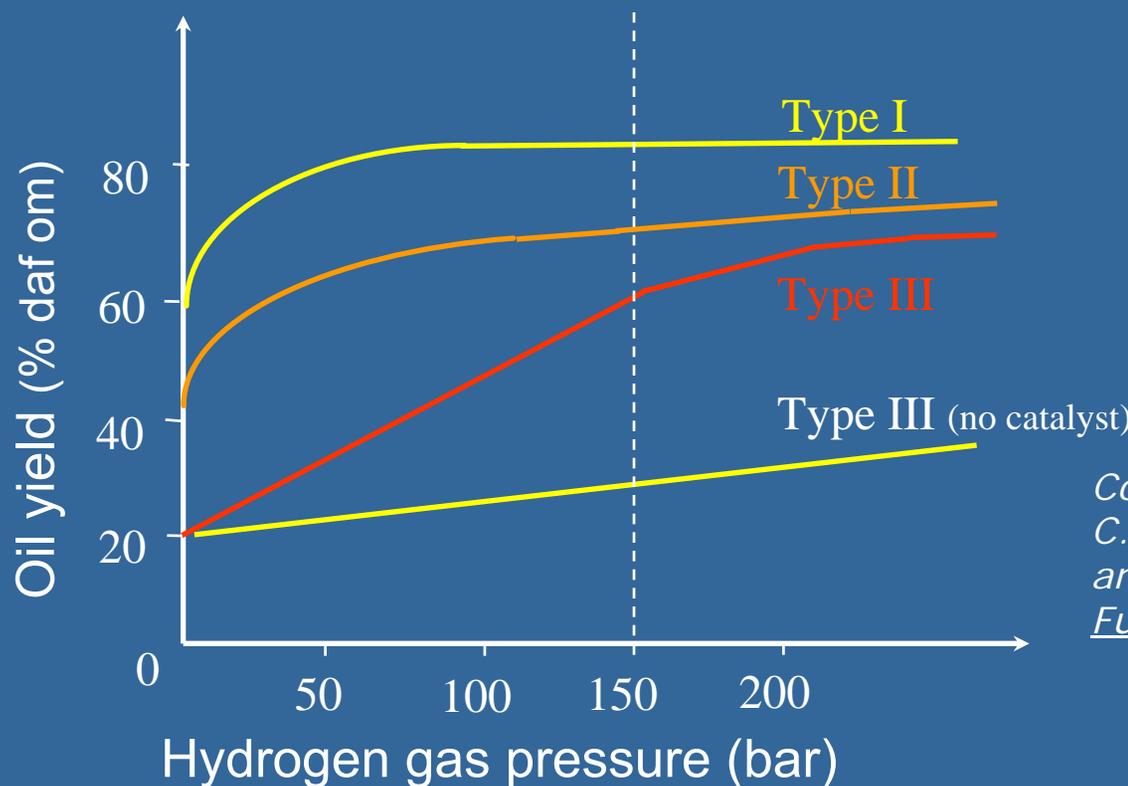
Catalytic Hydropyrolysis

- *hydrogasification with BTX production and then developed as a solvent-free coal liquefaction route*



Nottingham Fuel & Energy Centre

Oil yields - fixed-bed reactor (amb. - 520°C)



Compiled from :
Roberts et al.
(1994)

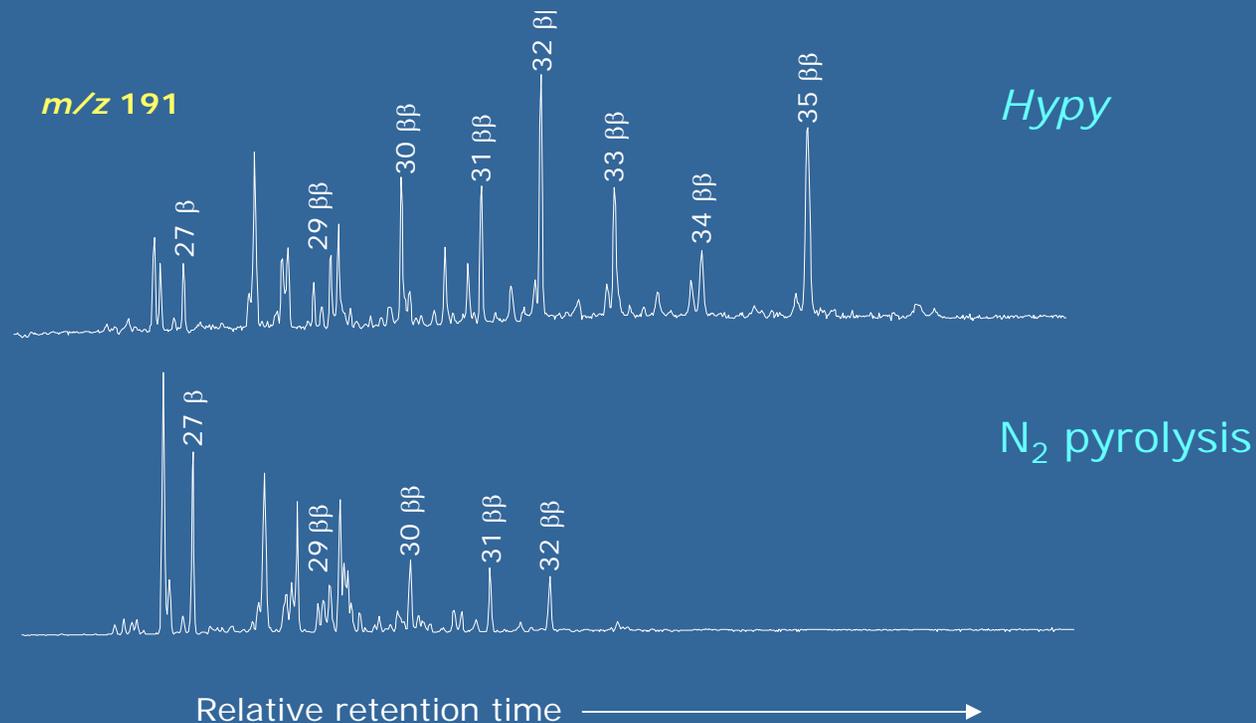
**High oil yields -
dispersed Mo catalyst**

Coal data adapted from:
C.E. Snape, C. Bolton, R.G. Dosch
and H.P. Stephens, *Energy &
Fuels*, 1989, 3, 421-425.

- Oil is dichloromethane-soluble, no pyridine sols/DCM insols.
- Conversions > 90% TOC for Type I and II kerogens.

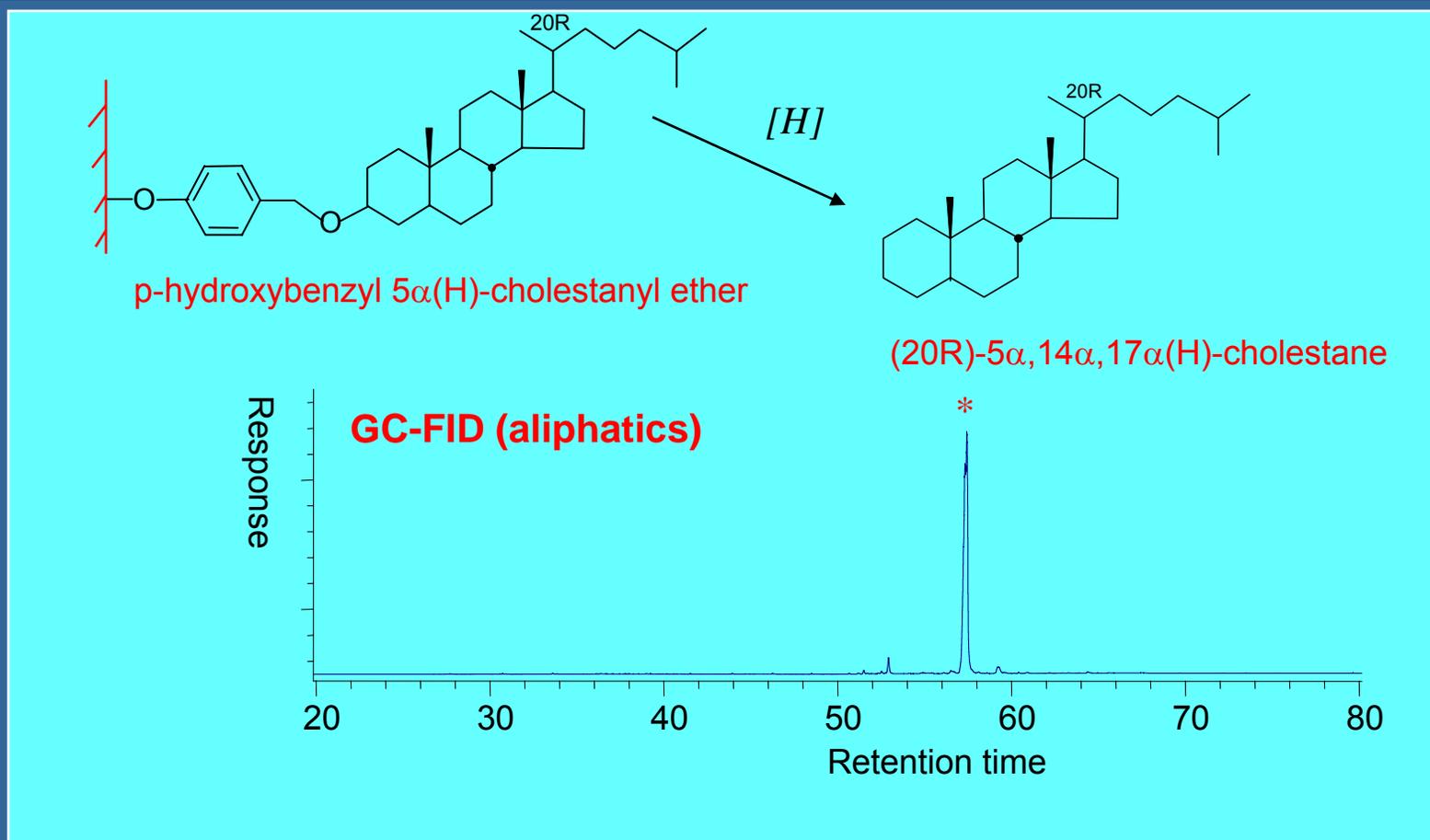
Effective release of bound biomarkers, e.g. hopanes, high H₂ pressure / catalyst/slow heating needed

- Pre-extracted recent sediment (Priest Pot UK) under different pyrolysis regimes.
- Similar results for immature source rocks.



G.D. Love, C.E. Snape, A.D. Carr and R.C. Houghton, The release of covalently-bound biomarker hydrocarbons via pyrolysis at high hydrogen pressure (hydropyrolysis), Organic Geochem., 1995, **23(10)**, 981-986.

Hypy of sterane-containing substrate demonstrating highly selective bond cleavage



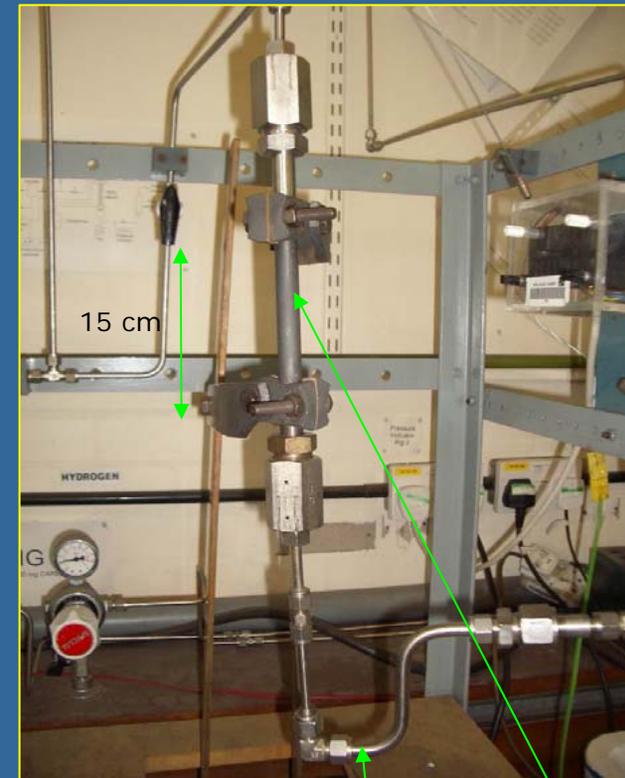
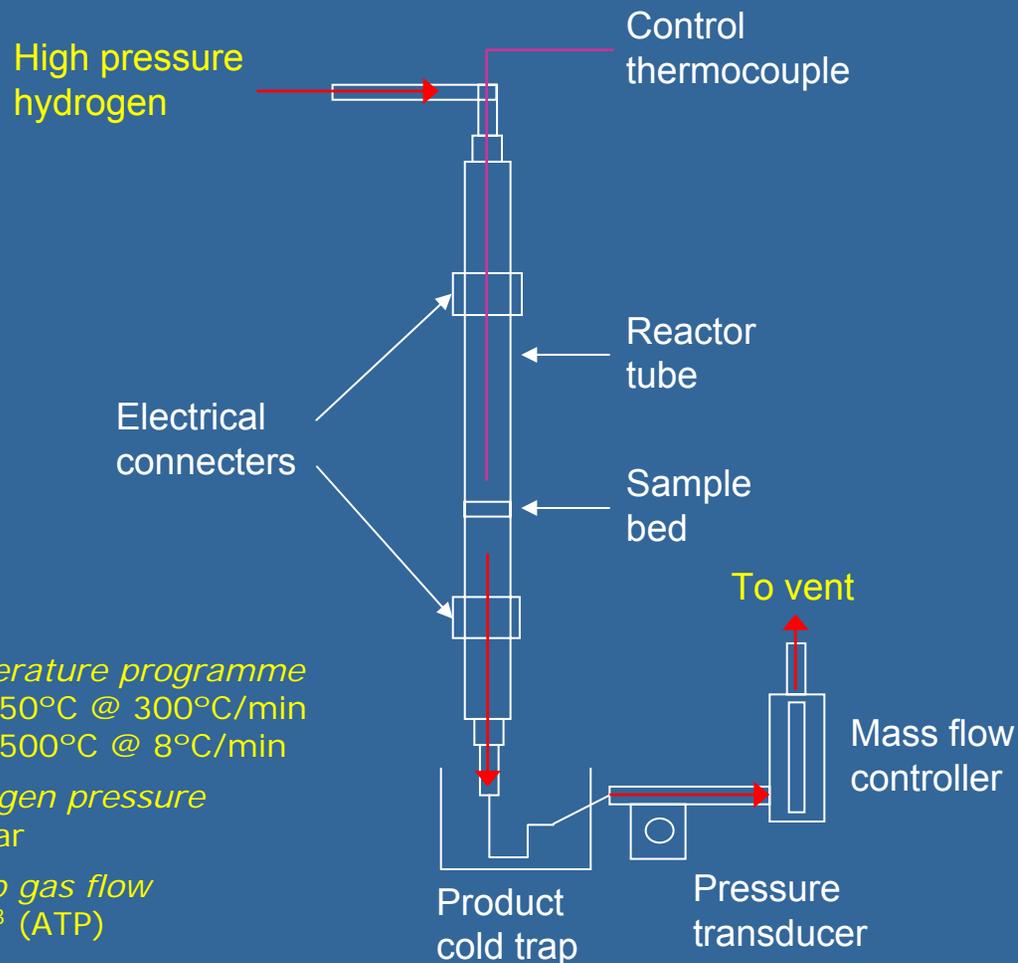
No discernible cracking or isomerisation of (20R)-5 α ,14 α ,17 α (H)-cholestane

Applications of hydrolysis in petroleum geochemistry/analytical pyrolysis

- **Bound biomarkers released via hydrolysis of asphaltenes and source rocks can potentially provide solutions to many problems in oil exploration.**
 - Accurate determination of maturity, source rock identification
 - Characterisation of biodegraded oils
 - Oil based mud contaminated source rock / reservoir cores
 - Oil field solids - tar mats and pyrobitumens
 - Reconstruct basin filling
- Carbonaceous chondrite meteorites - asteroid fragments from the formation of the Solar System 4.56 billion years ago - PAHs released via hpy.
- 2.5 billion year source rocks very H lean – late Archean age.
- Steroid defunctionalisation → stable C isotope ratios to detect administered endogenous steroids in urine.

Hydropyrolysis rig at Nottingham

- To handle mg quantities , size is important
getting smaller!

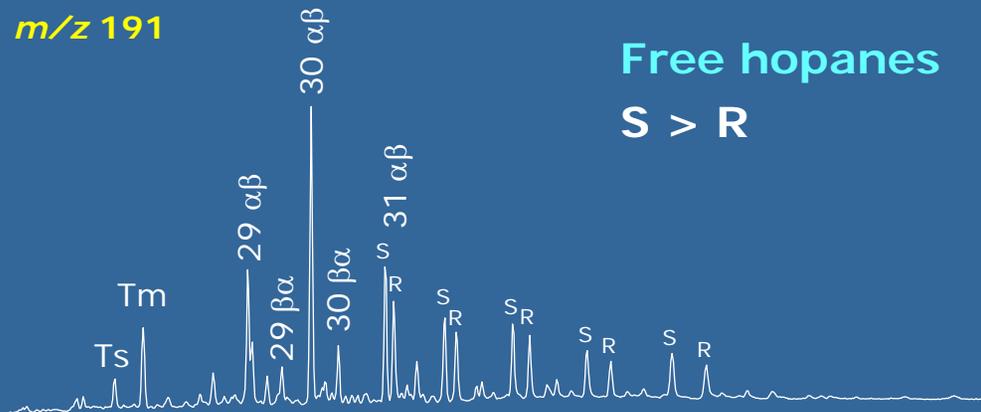


Improvements

- silica trap for oils.
- Asphaltenes – place on top of Mo catalyst.

Maturity assessment - free and hypy-released bound hopanes from the Kimmeridge Clay

m/z 191



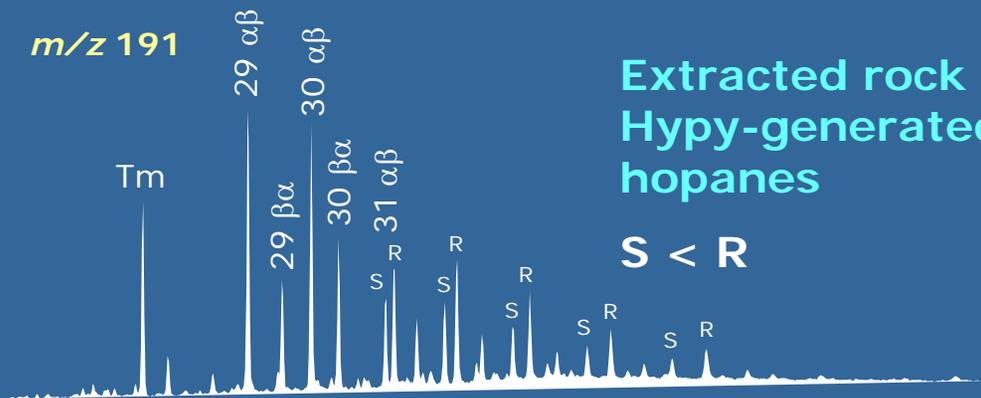
Free hopanes
 $S > R$



Kimmeridge Clay outcrop, Dorset (Jurassic)

Relative abundance

m/z 191

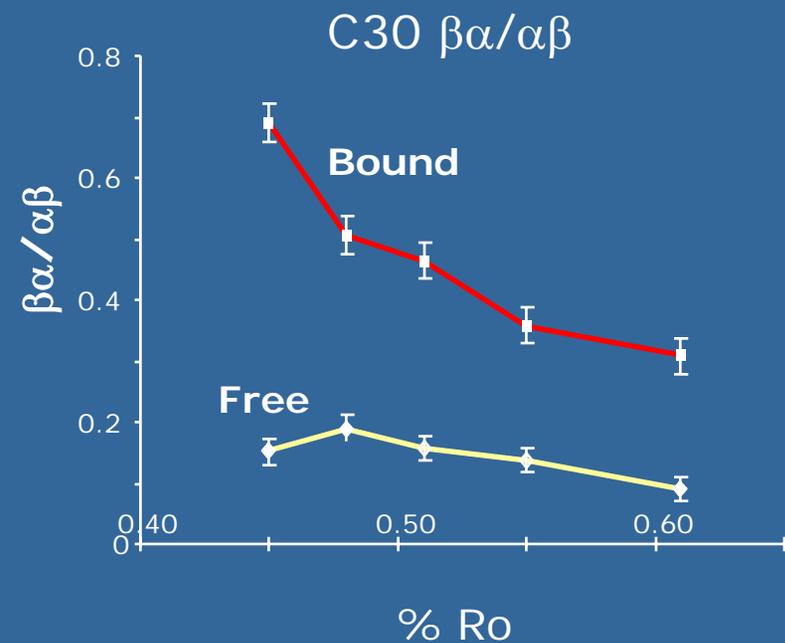
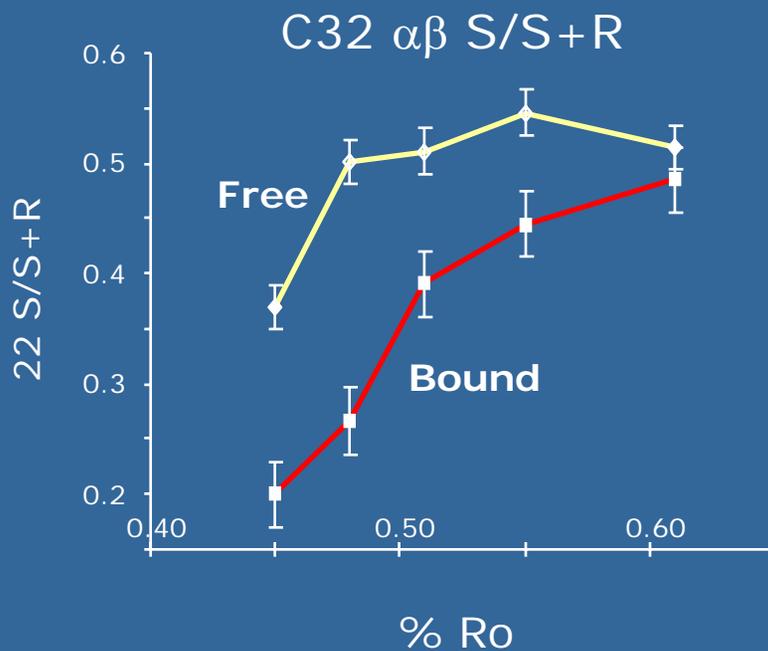


Extracted rock
Hypy-generated hopanes
 $S < R$

Relative retention time

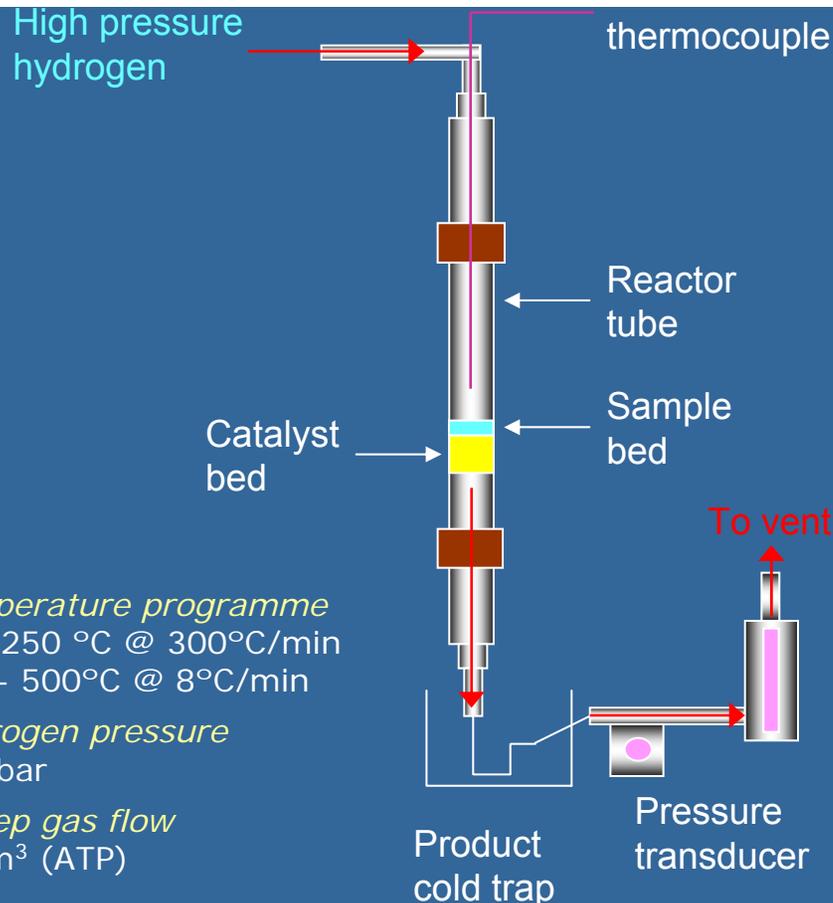
- Kimmeridge Clay (Central Graben, North Sea)
- The bound biomarkers released by hypy contain no Ts (or diasteranes)
- The bound biomarkers are less mature than their free counterparts, $R > S$, and $\beta\alpha$ isomers significantly more abundant than in the free phase

Maturity dependant biomarker ratios from a series of Kimmeridge Clay source rocks



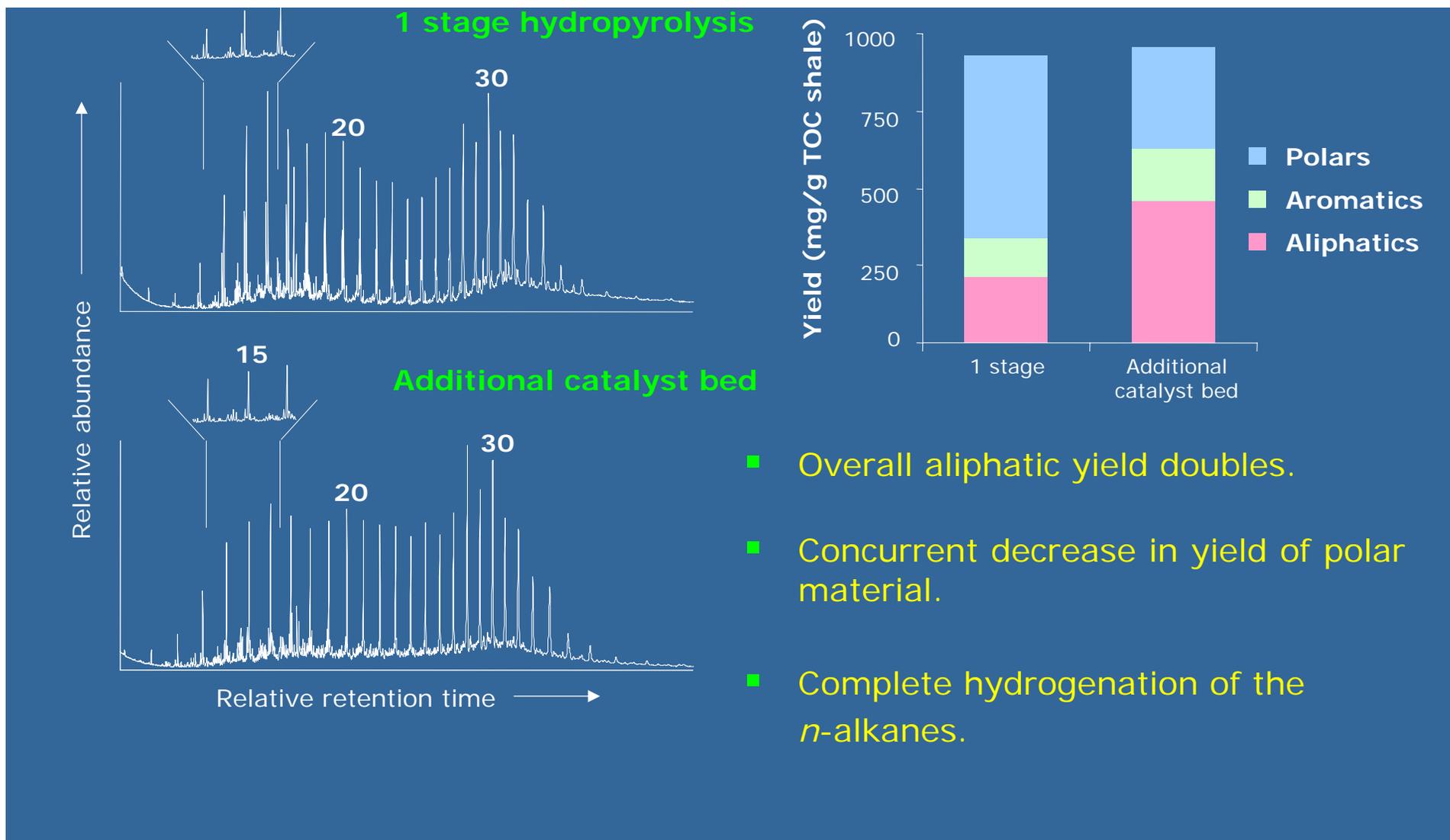
- Bound biomarkers undergo the same isomerisation reactions as their free counterparts, but the rates are retarded
- The maturity dependant biomarker ratios are valid over a wider range, and are more sensitive to relatively small changes in thermal maturity

Maximising the yield of aliphatic biomarkers via two-stage hydrolysis

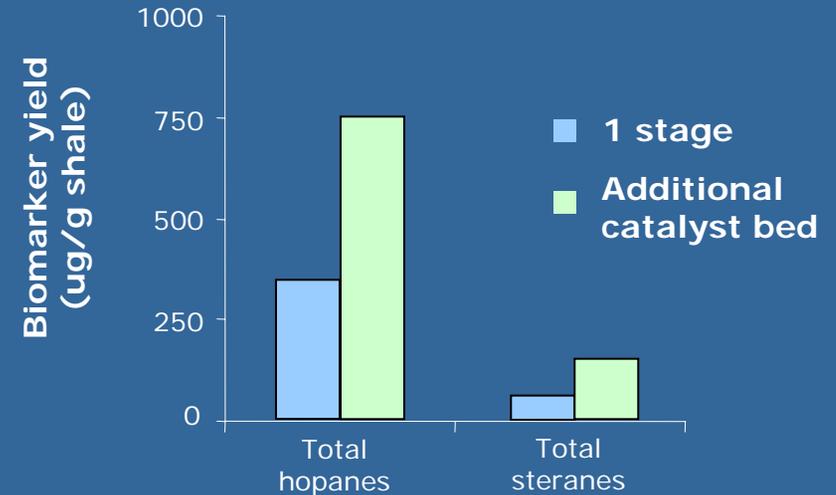
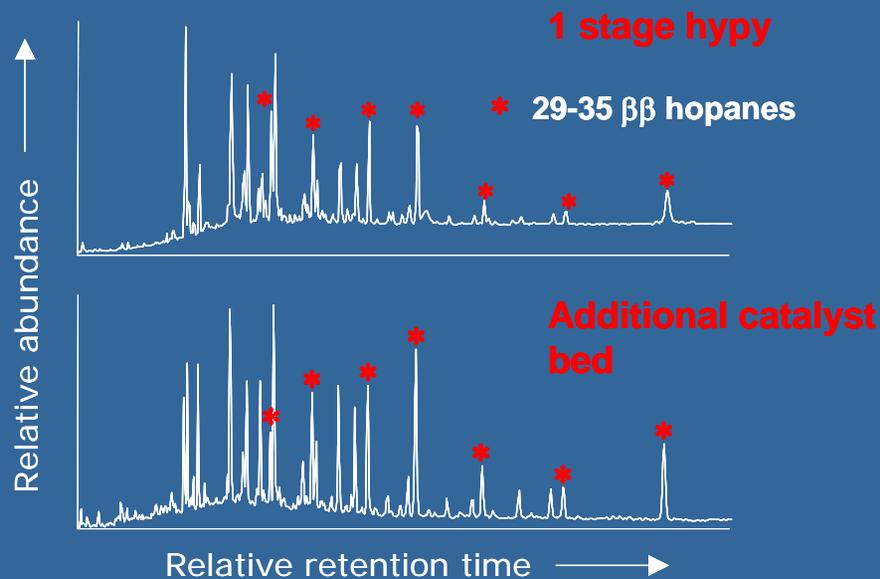


- Replacing the very active catalyst with a bed of the same sulphided Mo catalyst as in the 1st stage replicates the 2 stage results.
- As less active this catalyst can be placed directly below the catalyst and heated under the same temperature regime.
- Procedure is quicker and more reproducible than with the separate tube furnace.

Two stage hydrolysis of an immature Type I kerogen (Göynük Oil Shale, Turkey)



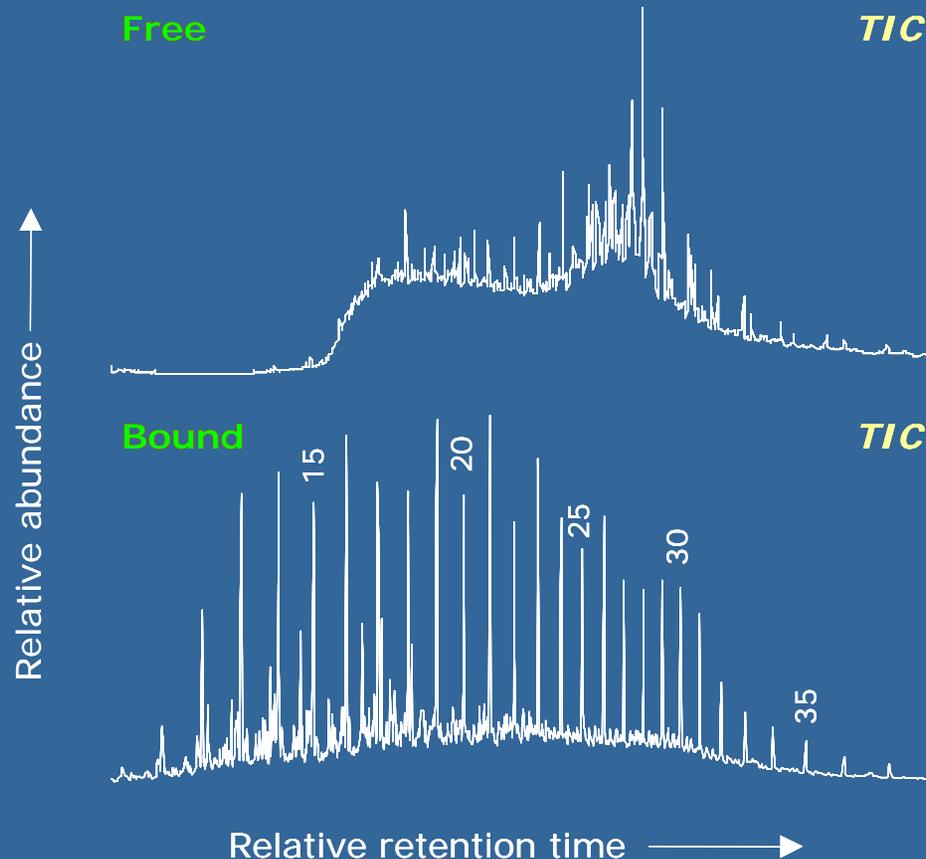
Two-stage hypy of Göynük Oil Shale - aliphatic hydrocarbon biomarker distribution



Ratio	1 stage	2 stage
C30 $\beta\alpha/\alpha\beta$ hopane	4.76	4.62
C31 $\alpha\beta$ S/S+R hopane	0.24	0.24
C29 $\alpha\alpha\alpha$ S/S+R sterane	0.05	0.06

- Total biomarker yield doubles
- High abundance of long chained thermodynamically unstable $\beta\beta$ hopanes suggests no significant cracking or isomerisation
- No effect on key maturity dependant biomarker ratios

Hypy of asphaltenes isolated from a biodegraded crude oil



- Soldado oil (Trinidad), moderate biodegradation has removed all of the *n*-alkanes and isoprenoids from the free phase.
- Hypy of oil asphaltenes generates a pristine *n*-alkane profile.
- Important source specific characteristics of the oil revealed.

Deciphering Reservoir Filling History

The Hypothesis

- The most strongly bound phase, the asphaltenes for a particular section of core rock is representative of the first oil charge to contact the rock.
- Accessing the biomarkers bound to the adsorbed phase gives information as to the character of the oil at the time of generation/migration.
- Concept proven in laboratory displacement experiments of one oil by another on dry and wet sand.
- Mapping the maturity of the biomarkers bound most strongly to the adsorbed phase along the reservoir structure gives information on relative migration directions.

C.A. Russell, W. Meredith, C.E. Snape, G.D. Love, E. Clarke and B. Moffatt, The potential of bound biomarker profiles released via catalytic hydrolysis to reconstruct basin charging history for oils, Organic. Geochem., 2004, 35(11-12), 1441-1459.

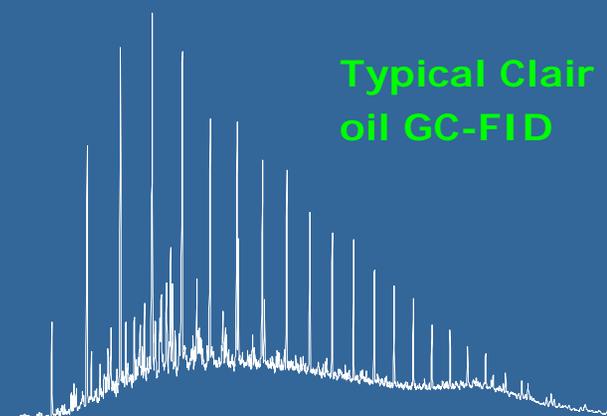
Clair field

Oil geochemistry and *previous studies*



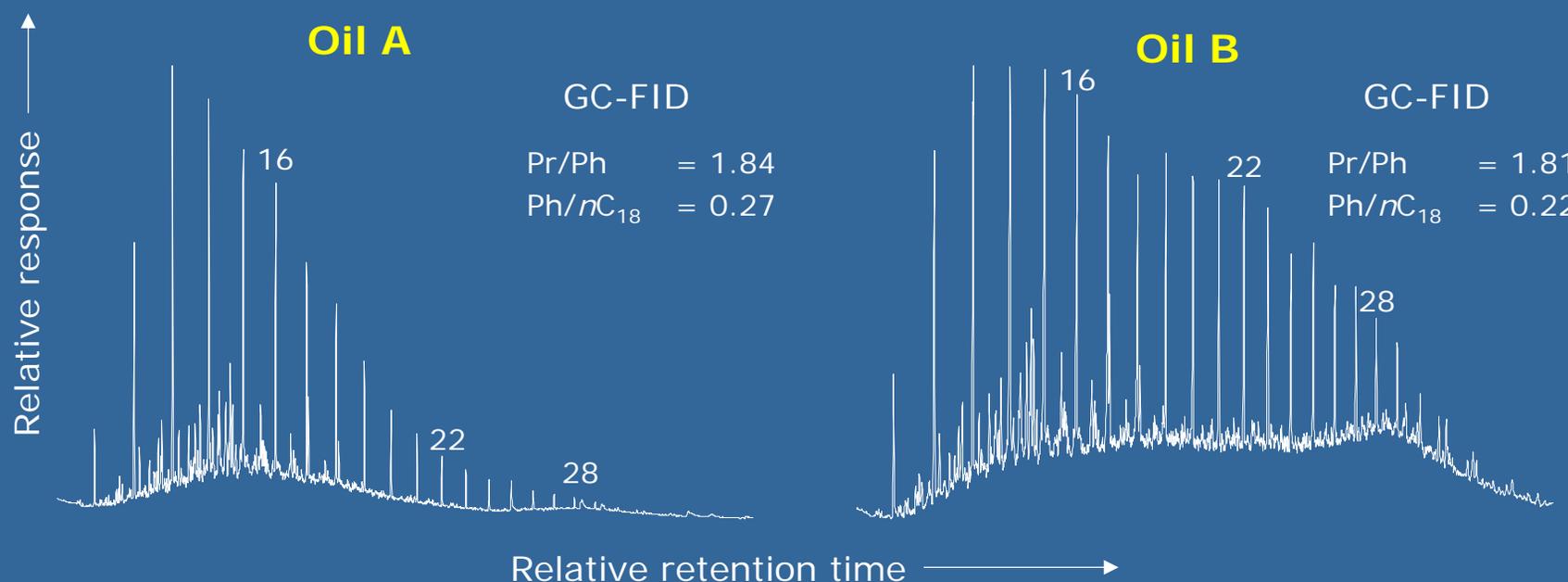
- Discovered 1977 – 75 km west of Shetland
- Largest accumulation on UKCS
 - 3-5 billion barrels in place
- Field covers 5 blocks
 - 206/7a, 206/8; 206/9; 206/12 and 206/13a
- Reservoired in sandstones of Devonian to Carboniferous age
- Began producing early 2005

- Thought to be a mixture of two distinct oil charges - first heavily biodegraded
 - ⟨ Relatively low API ~ 22-24
 - ⟨ High acidity - TAN ~1.2 (mg/ KOH/g)
 - ⟨ UCM below chromatogram baseline
 - ⟨ Presence of *n*-alkanes and 25-norhopanes



Clair Oil Samples

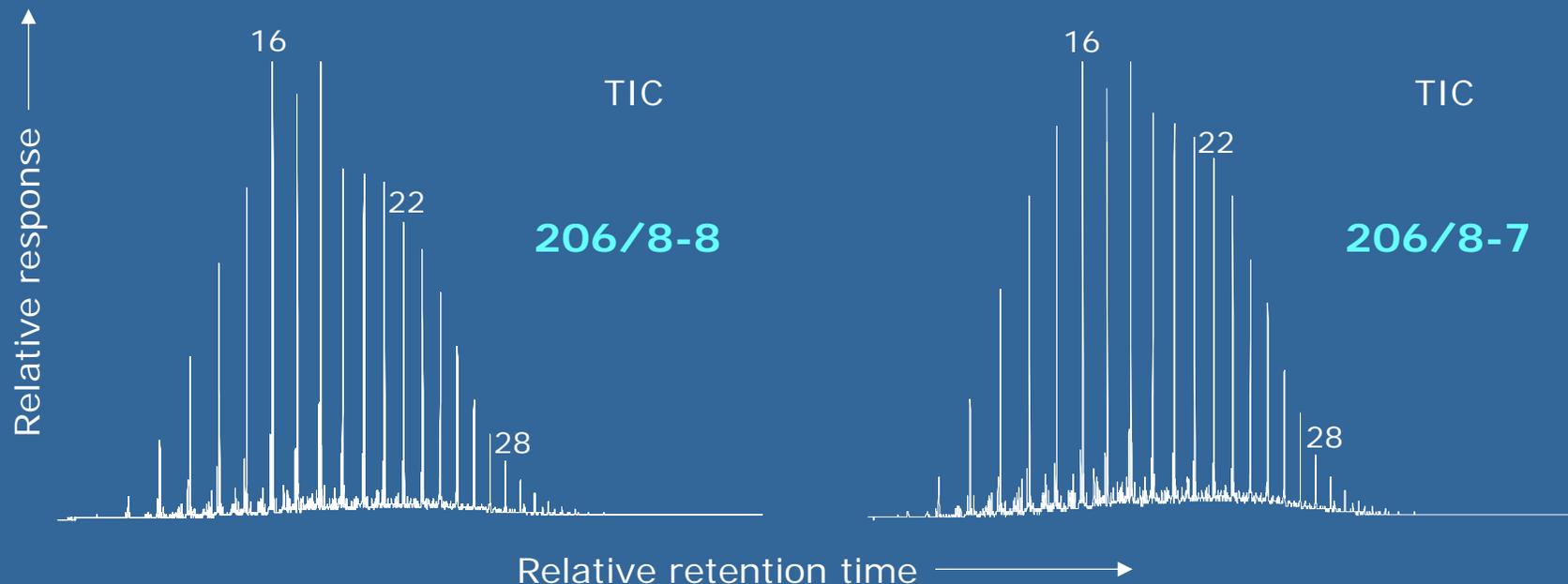
Free *n*-alkane distributions



- *n*-alkanes profiles very variable

Oil stained core samples

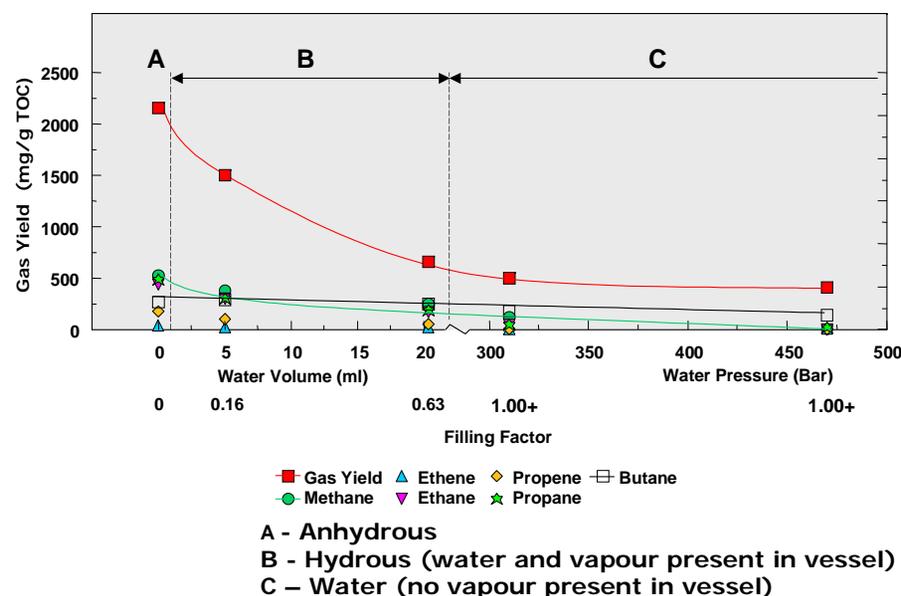
Distributions of bound n-alkanes released by hypy



- *n*-alkane profiles very similar with no variation between wells.
- These asphaltenes are thought to represent the first oil charge to encounter the reservoir core.
- Initial oil charge was waxy and single sourced - lacustrine input.
- Stable carbon isotopes suggests Devonian rather than later Jurassic source.

Can pressure severely retard cracking (volume expansion) processes, such as oil cracking to gas?

Oil cracked for 350°C for 24 hours



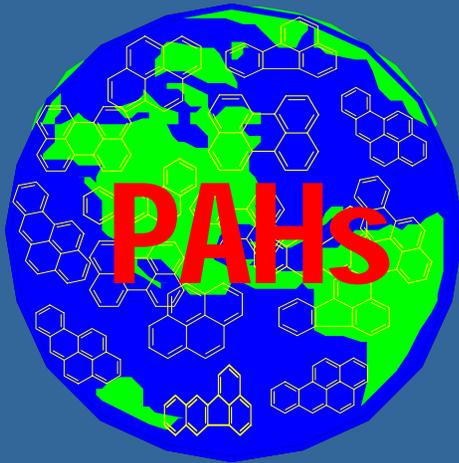
- Theory indicates that both kinetics and thermodynamics are affected.
- However, pressure is considered only to have a secondary on oil generation and cracking
- Problem is due to nature of experimentation – true confined liquid pressure medium not employed.

■ Results at moderate liquid pressures (150-500 bar) indicates that light hydrocarbon gas suppressed both by phase change to liquid (B) and then by increasing liquid pressure (C).

■ ***Explains why oil survives in high T and P geological basins.***

Fossil Fuel Utilisation

the major source of PAHs in the environment



- Ubiquitous toxic and cancer-producing contaminants in the environment
- Arise both naturally and anthropogenically
- Elevated concentrations in sedimentary environments post-dating the industrial revolution strongly demonstrated the '**DEEP IMPACT**' of enhanced fossil fuel utilisation.

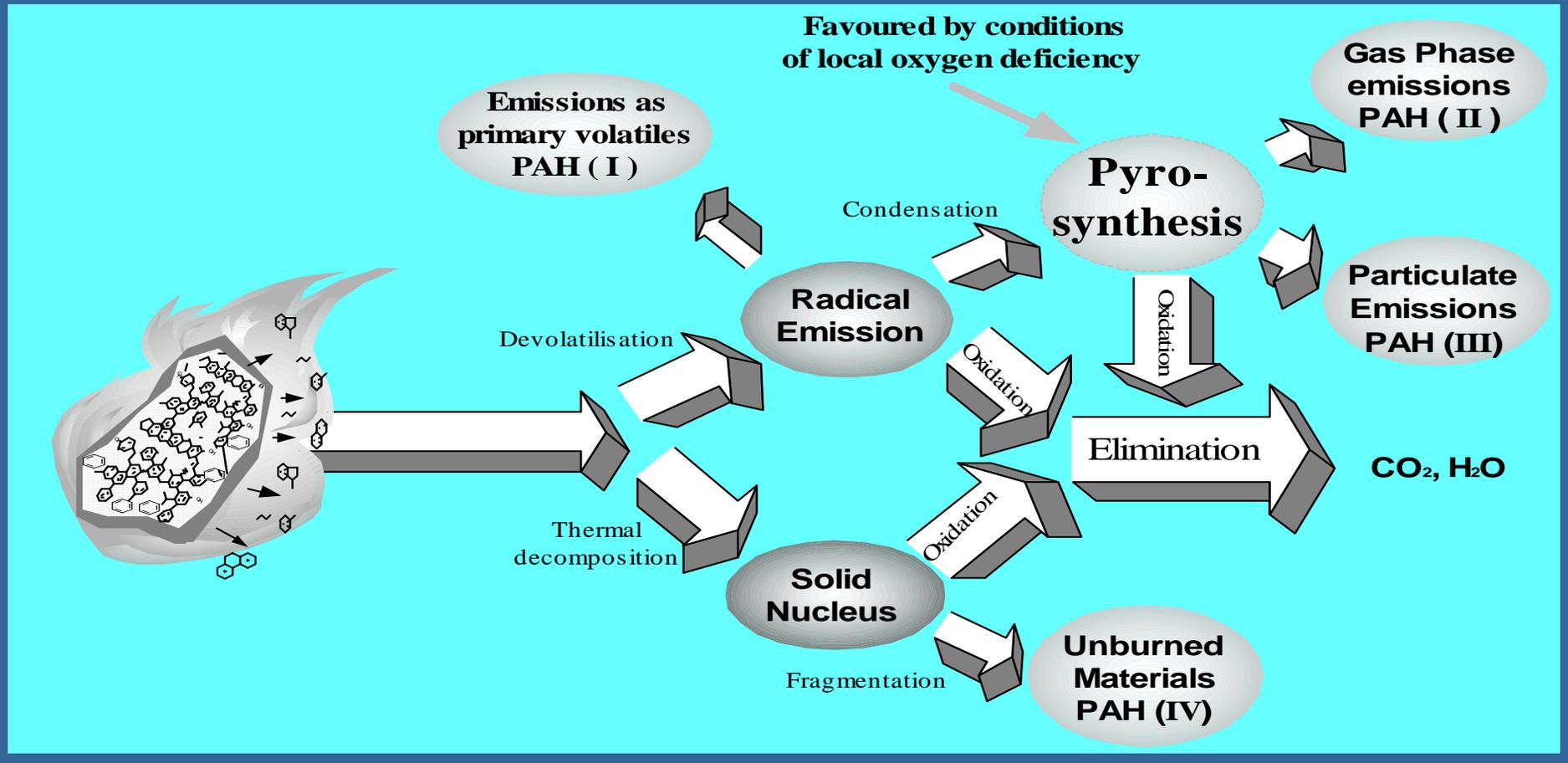
Multiplicity of PAH-contributing sources

- ◆ *Industrial/domestic facilities consuming coal/petroleum and their derived products*
- ◆ *Oil/oil transportation industry*
- ◆ *vehicle exhausts and air traffic sources*
- ◆ *Domestic/commercial/industrial natural gas utilisation*
- ◆ Wood/biomass utilisation
- ◆ Agricultural burning
- ◆ Waste incineration

Chemistry of PAH formation during combustion/carbonisation

Two basic origins:

- (1) Release as (primary) fuel components
- (2) Pyro-synthetic reactions



The need of new techniques for PAH source apportionment

- **Why conclusive source apportionment cannot be achieved by conventional molecular approaches ?**
 - General molecular similarities of PAH emissions from a large variety of sources
 - Physical and biogeochemical factors that may neutralise or eliminate the molecular features that are believed to indicate their sources.
 - Variable liability of different PAHs to photo-oxidation, biodegradation and their biogeochemical factors.
- **Compound-specific stable isotope measurements**
 - *Stable isotope ratios characteristic of source, provided no significant change occurs on bio/phytoremediation.*

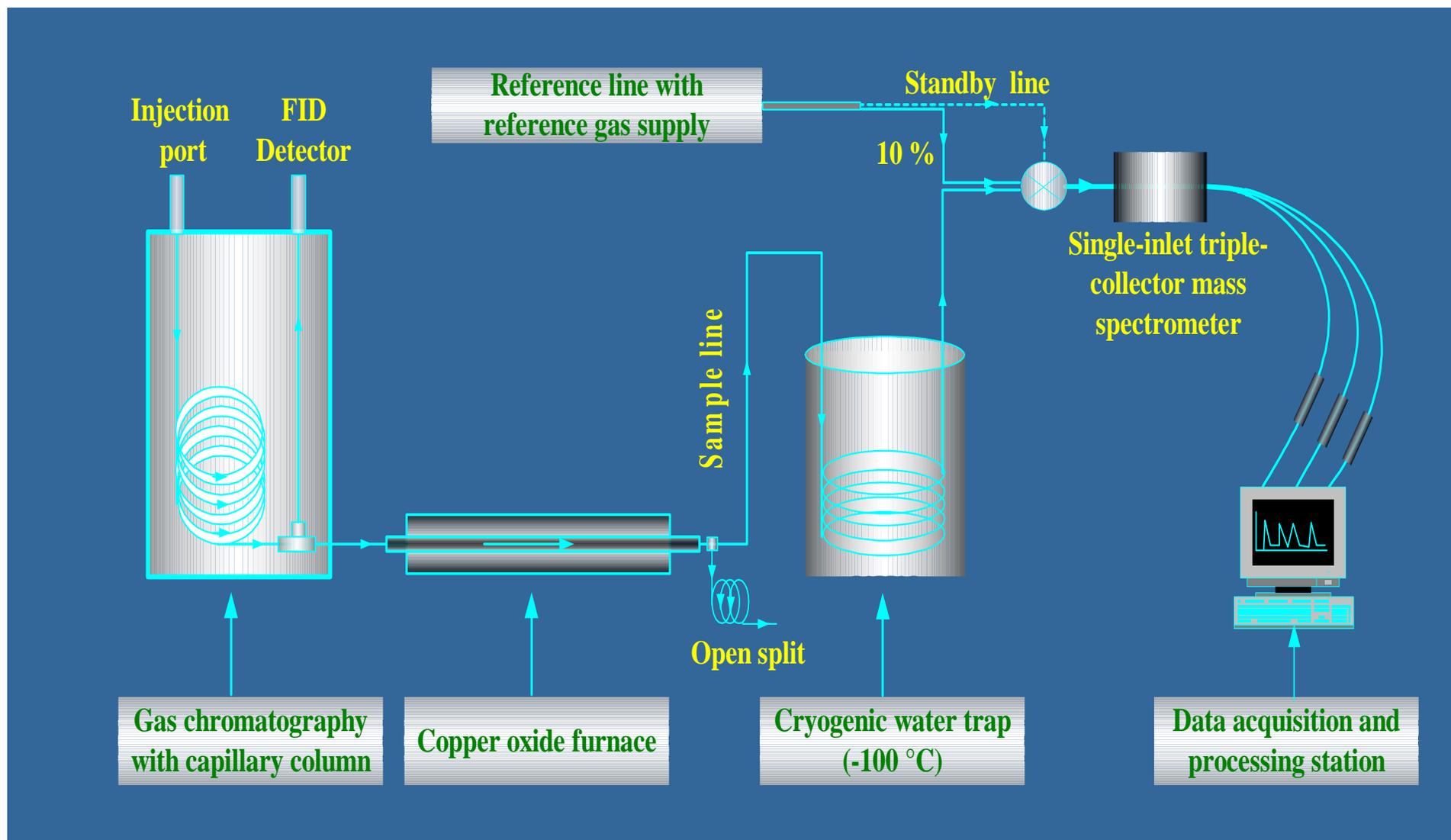
BACKGROUND ON STABLE CARBON AND HYDROGEN ISOTOPES

- **Compounds of biological origin are always enriched in the lighter ^{12}C isotope as opposed to the heavier ^{13}C .**
- **Fossil fuels, i.e. coal, petroleum and natural gas, are often isotopically distinguishable:**

	$\delta^{13}\text{C}$ (‰, PDB)	δD (‰, SMOW)
Crude oil: mainly	-27 ~ -28‰	-90 ~ -180
Coal:	-23 ~ -25‰	-60 ~ -120
Natural gas (CH_4):	-55 ~ -110‰	-170 ~ -400

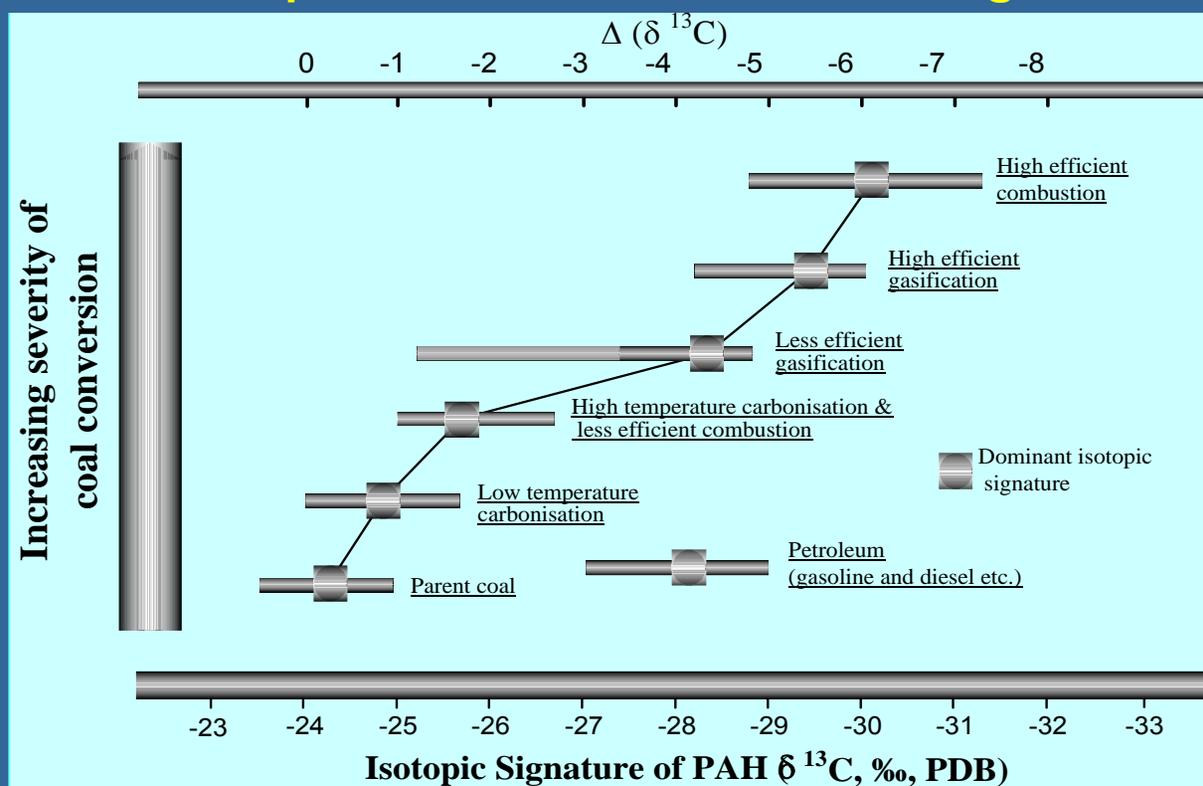
- **Ubiquitous compounds from different sources may exhibit varying isotopic compositions relative to each source.**

Schematic of a GC-IRMS System



Why is $\delta^{13}\text{C}$ CSIA technology special in sourcing or tracking the journey of PAH emissions?

1. Source-unique $\delta^{13}\text{C}$ isotopic profiles for different sources
2. Highly responsive to different PAH formation mechanisms.
3. Little isotopic fractionation occurs during environmental degradation.



C. McRae, C.E. Snape and A.E. Fallick, *The Analyst*, 1998, 123, 1519-1522.

C. McRae, C-G Sun, C.F. McMillan, C.E. Snape and A.E. Fallick, *Polycyclic Aromatic Compounds*, 2000, 20, 97-109.

C. McRae, C-G Sun, C.E. Snape and A.E. Fallick, *Organic Geochem.*, 1999, 30, 881-889.

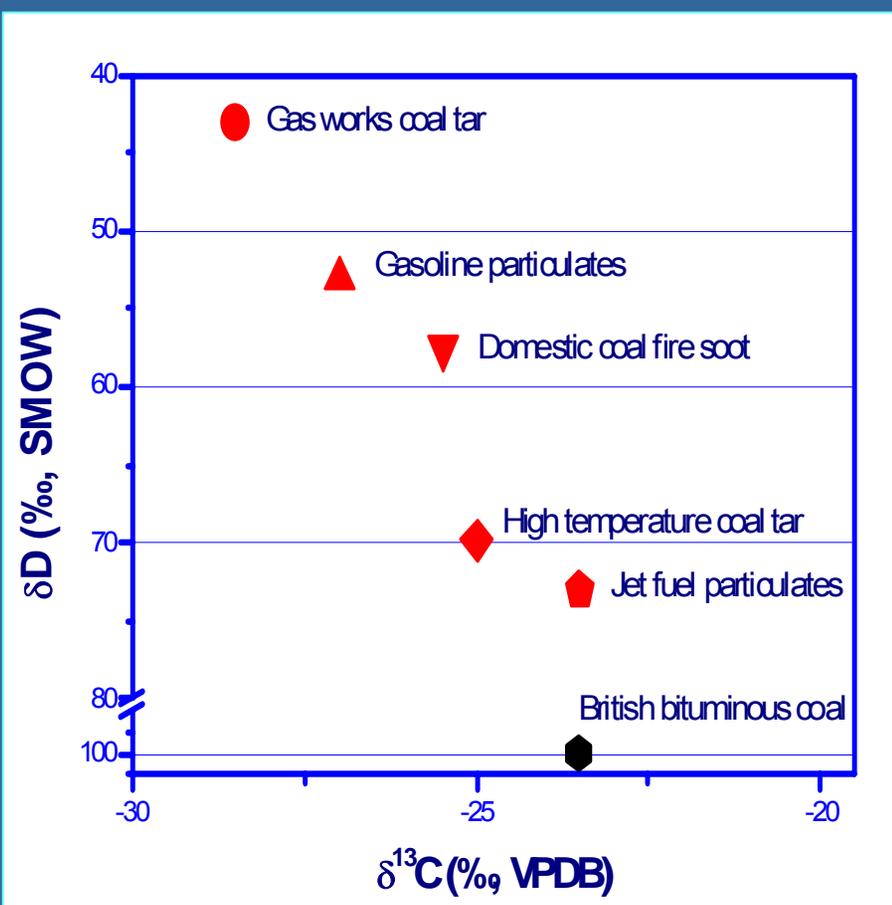
Thanks to Tony Fallick.

Natural gas (CH_4)

-35 ~ -64 ‰

The combined use of $\delta^{13}\text{C}$ and δD measurements makes PAH source apportionment more conclusive

Correlation of $\delta^{13}\text{C}$ and δD for selected PAHs from typical different sources

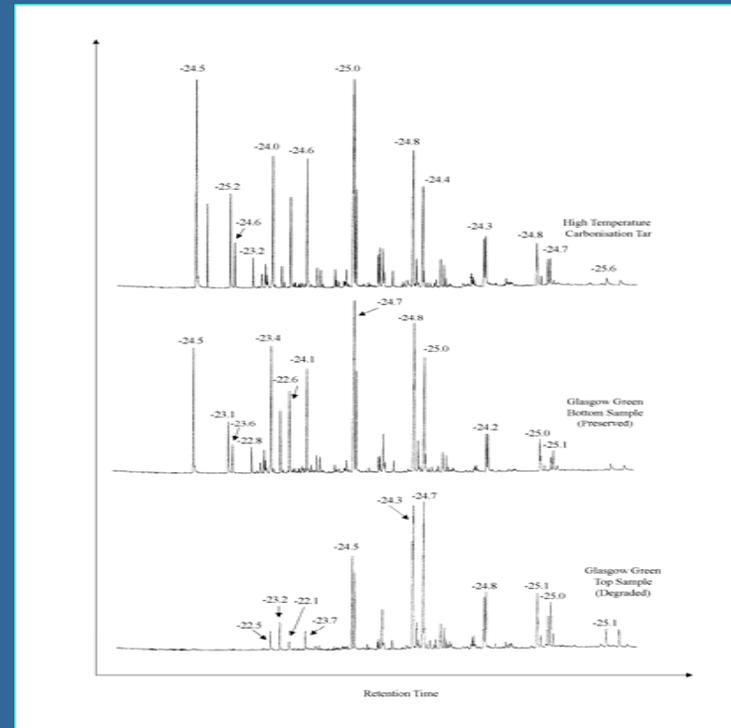


■ Differences of ca 40 ‰ in δD values between different sources and variations of up to 20 ‰ between PAHs from single sources were observed.

■ The wider range of δD values, if taken with $\delta^{13}\text{C}$ signatures, provides a much greater degree of differentiation between PAHs from different sources.

C-G Sun, M. Cooper and C.E. Snape, Use of compound-specific $\delta^{13}\text{C}$ and δD stable isotope measurements as an aid in the source apportionment of PAHs, *Rapid Comm. in Mass Spectrometry*, 2003, 17, 2611-2613.

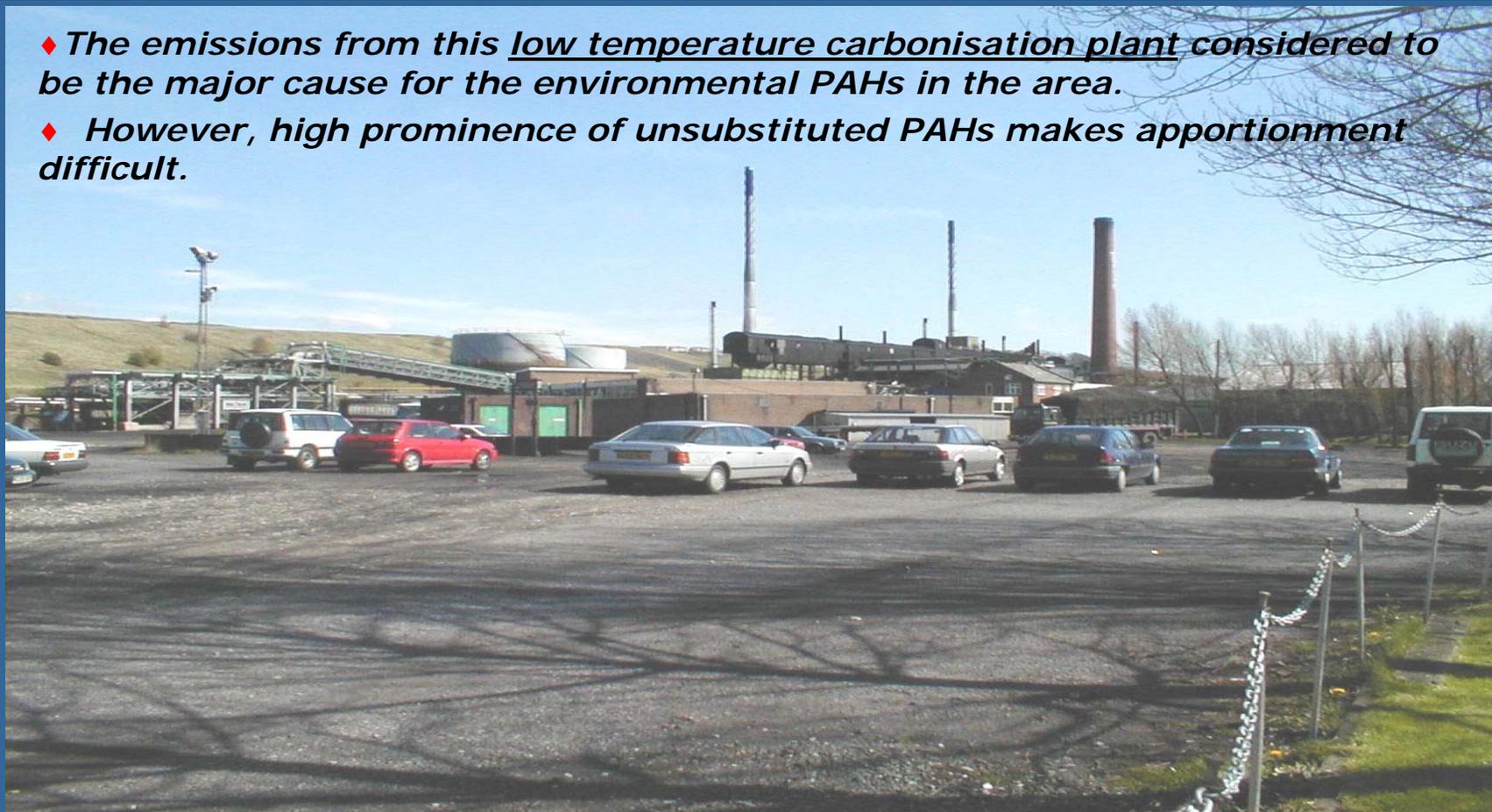
Glasgow Green Site



- *Illegal tar dumping – either from gas works or coking plant in a former air swimming pool*
- ***Close match to high T coal tar in PAH distribution and isotopic ratios (-25 ‰).***

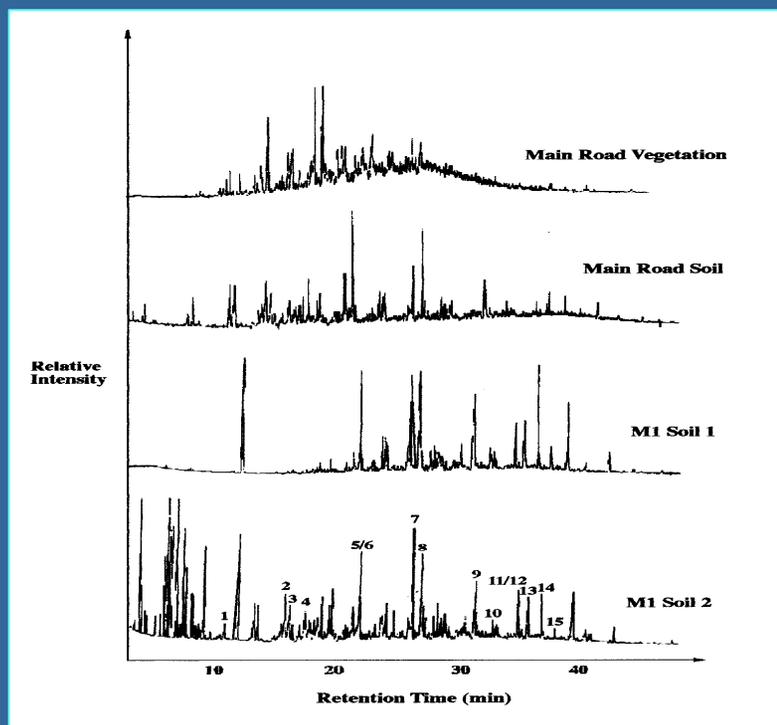
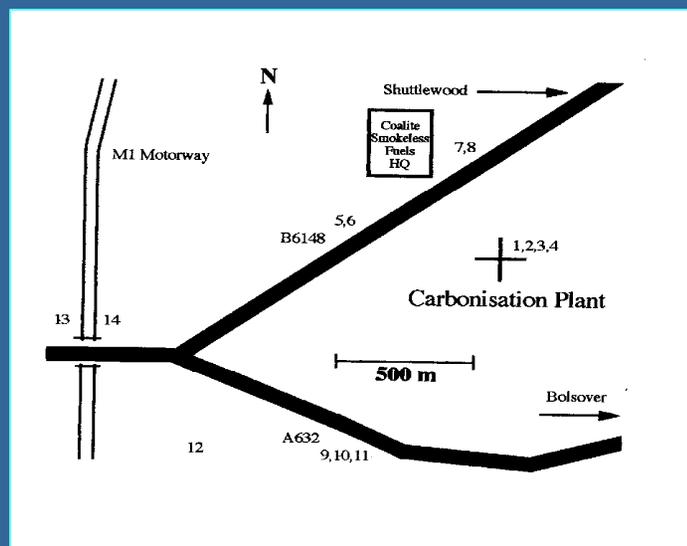
Low temperature carbonisation plant, Bolsover, North Derbyshire

- ◆ *The emissions from this low temperature carbonisation plant considered to be the major cause for the environmental PAHs in the area.*
- ◆ *However, high prominence of unsubstituted PAHs makes apportionment difficult.*



C-G Sun, C.E. Snape, C. McRae and A.E. Fallick, *Resolving coal and petroleum-derived polycyclic aromatic hydrocarbons (PAHs) in some contaminated land samples using compound-specific stable carbon isotope ratio measurements in conjunction with molecular fingerprints*, *Fuel*, 2003, 82, 2017-2023.

GC profiles of aromatics from vegetation and soil samples



Generally, little resemblance to low T coal tar

- However, many isotopic values in range -24 to -26 ‰.
- Parent PAH present – may suggest another source, e.g. high T carbonisation?
- High MM PAH exhibit isotopically lighter signatures (< -28 ‰) suggesting transport fuel/biomass contribution.

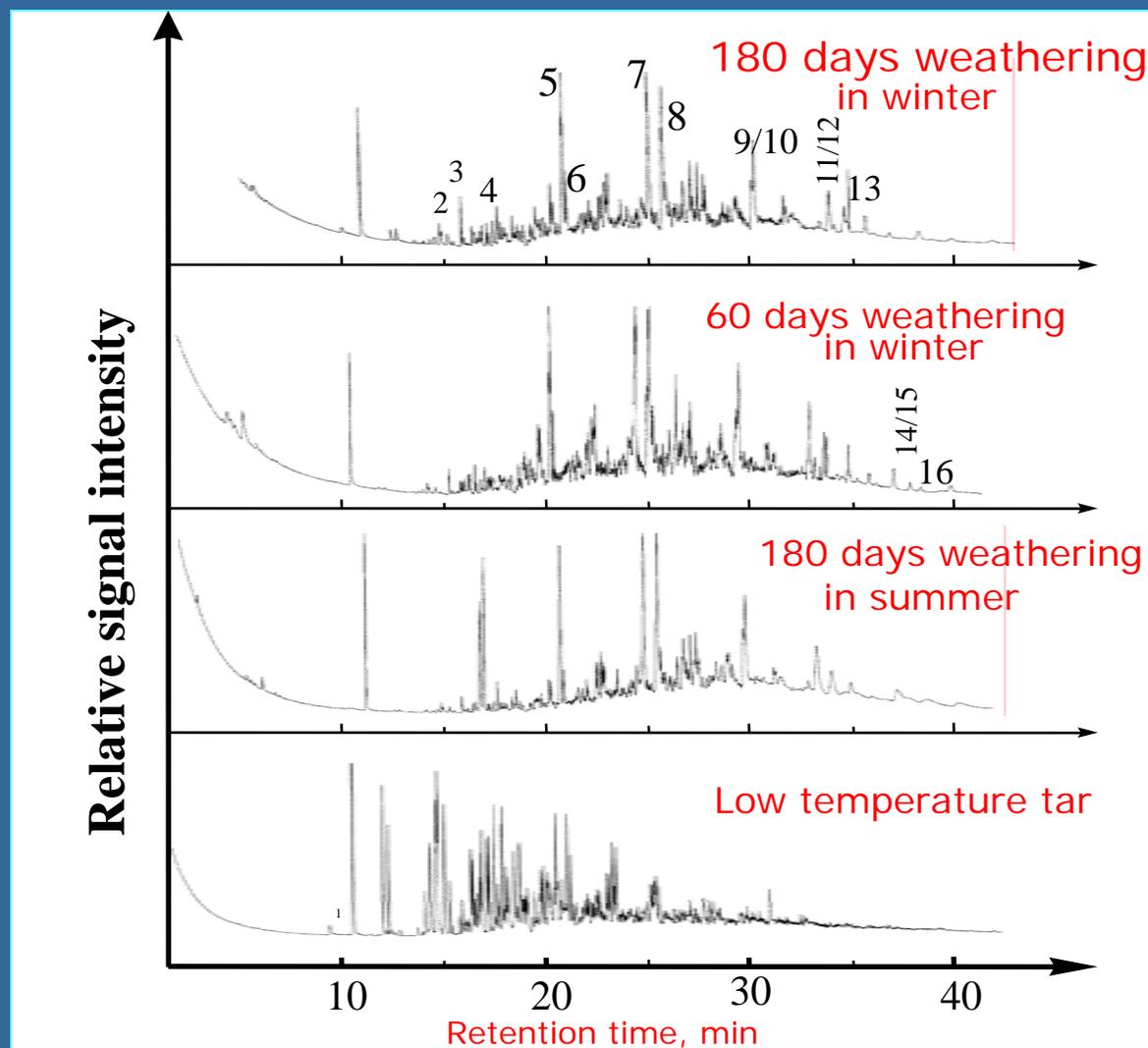
GC profiles of neutral aromatics from weathered and initial low temperature coal tar



The University of Nottingham

Alkyl substituted PAHs degrade faster than parent PAHs overshoot periods, but carbon stable isotopic values remain constant close to -25 permil.

Nottingham Fuel & Energy Centre

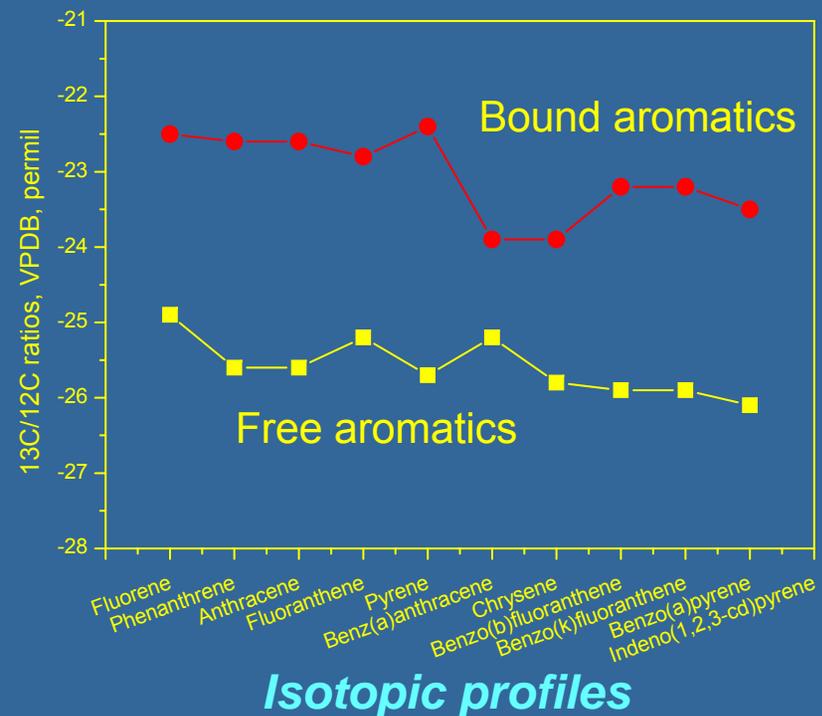
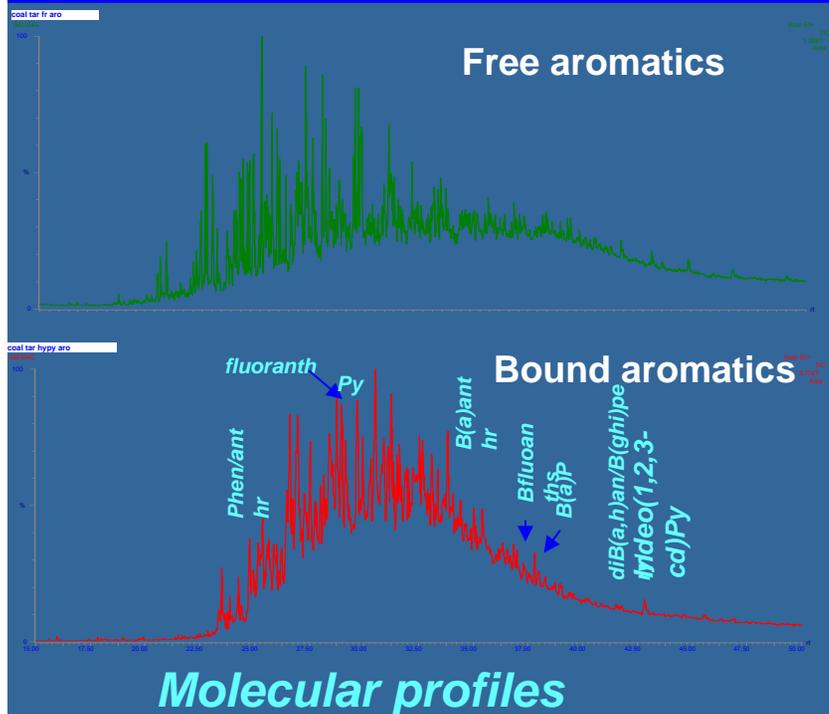


- 4. Fluorene
- 5. Phenanthrene
- 6. Anthracene
- 7. Fluoranthene
- 8. Pyrene
- 9. Benz(a)anthracene;
- 10. Chrysene
- 11. Benzo(b) Fluoranthene
- 12. Benzo(k) fluoranthene
- 13. Benzo(a) pyrene
- 14. Dibenz(a,h) anthracene

Low temperature coal tar

The molecular and isotopic profiles of free and asphaltene-bound aromatics

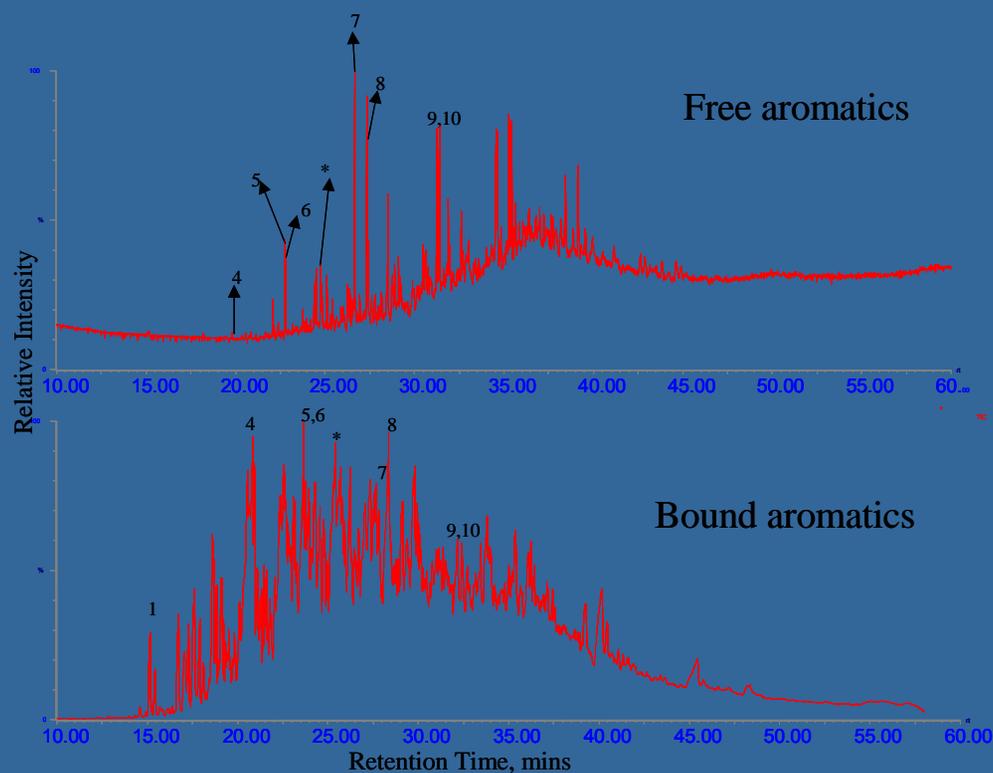
- ◆ Molecular compositions of hypy released asphaltene-bound and free aromatics are similar, both heavily alkyl-substituted.
- ◆ The bound aromatics released by hypy are more enriched in ^{13}C than the free ones by 1-3 ‰, having $\delta^{13}\text{C}$ values (22.5 ~ 23.7 ‰), similar to those for coals (-23 ‰).



A soil sample from close to the low temperature carbonisation plant

- Both the molecular and the isotopic profiles for the bound aromatics are consistent with low rather than high temperature tar being the major input.
- For the free aromatics, the presence of prominent parent PAHs, with a coal origin, must arise from the preferential degradation of alkylated constituents.

$^{13}\text{C}/^{12}\text{C}$ isotope ratios, ‰ VPDB

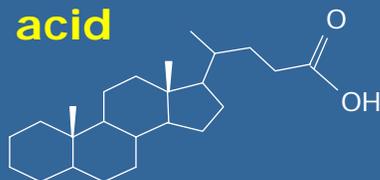


PAHs	Free aromatics	Bound aromatics
4. Fluorene	-22.5	-20.5
5. Phenanth	-22.7	-19.7
6. Anthr	-22.7	-19.7
7. Fluoranth	-24.8	-19.9
8. Pyrene	-24.7	-23.3
9. Benz(a)anthr	-25.4	-22.8
10. Chrysene	-25.4	-22.8
11. Benzo(b)fluoranth	-25.2	-22.0
12. Benzo(k)fluoranth	-25.2	-22.0
13. Benzo(a)py	-24.4	-22.2
14. Indeno(1,2,3-cd)py	-26.6	-23.3
15. Dibenz(a,h)anthr	-26.6	-23.3

5 β -cholanic acid

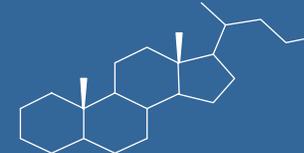
*-highly selective defunctionalisation using
hypy to 5 β -cholane*

5 β -cholanic acid



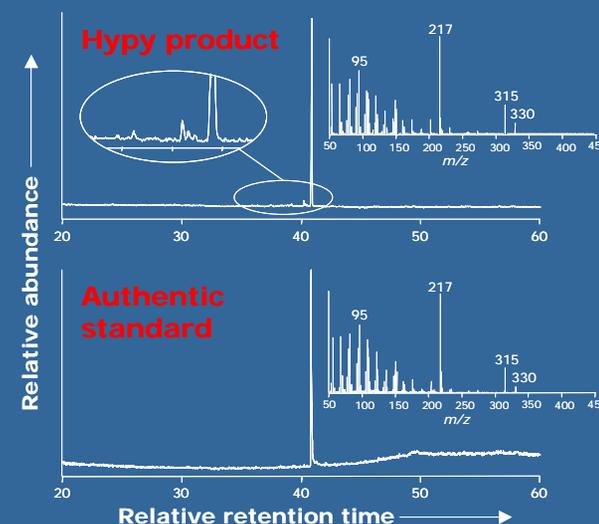
$\delta^{13}\text{C}$ (‰) - 14.6

5 β -cholane



$\delta^{13}\text{C}$ (‰) - 14.7

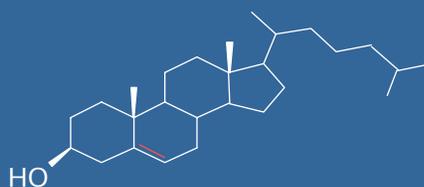
- >95% of the product is 5 β -cholane, with a spectra identical to that of an authentic standard.
- The $\delta^{13}\text{C}$ values are similar for both the carboxylic acids and defunctionalised alkanes.
- Again there is no significant isotopic fractionation during hydropyrolysis.



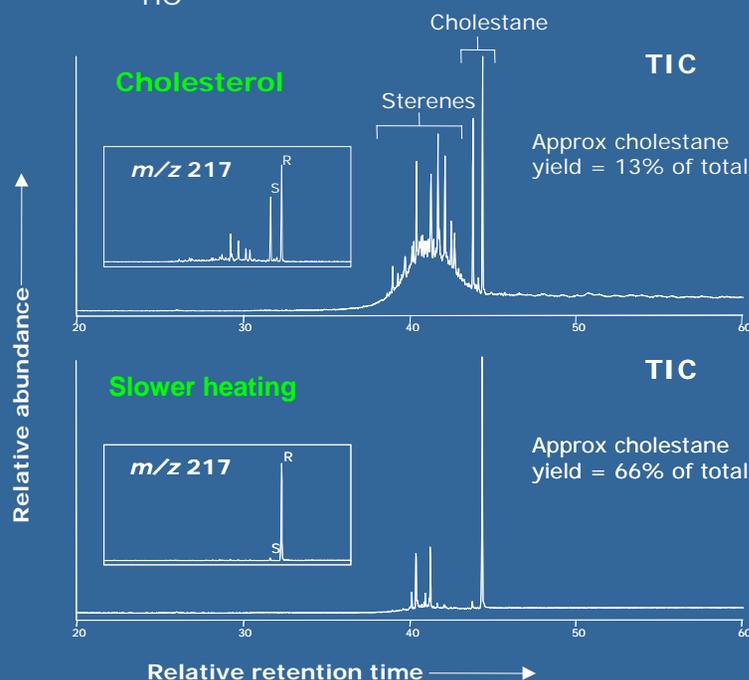
Rapid prep. method for steranes.

If this selective defunctionalisation works on steroids – will facilitate carbon stable isotopes to detect administered endogenous steroids in urine.

Cholesterol



Cholestane

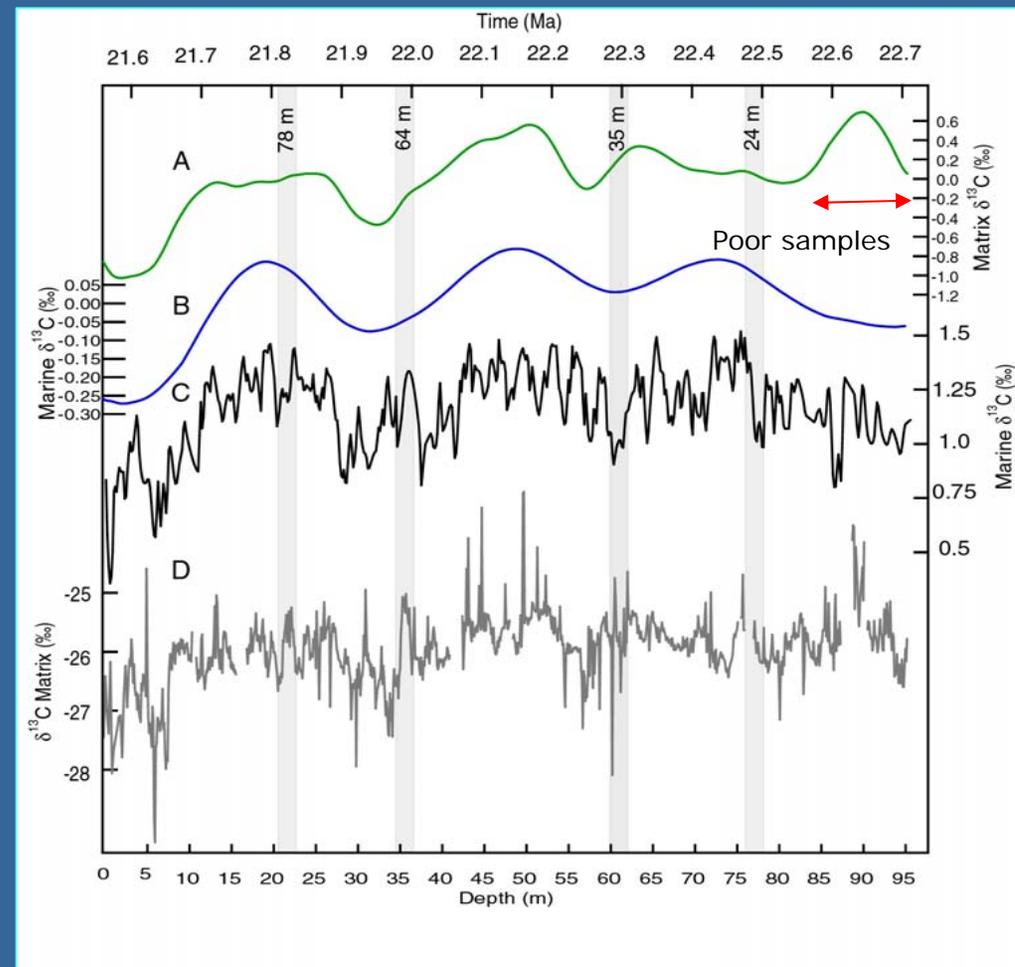


- Lower selectivity with the functional group on the ring system rather than the side chain
- Double bond migration in cholesterol results in generation of sterenes at temperatures below the activation point of the catalyst - saturated cholestanol generated fewer sterenes
- With the double bond adjacent to a ring joining position two isomers are inevitable - for cholestanol only the R isomer is produced

Correlation between Morwell brown coal and marine $\delta^{13}\text{C}$ records

- lignite record was compared to a marine carbonate record for the first time

- Both records display evidence of similar long-term oscillations of the earth and a general decrease in $\delta^{13}\text{C}$ of the exogenic carbon reservoir between 22.6 and 21.5 Ma.
- However, the terrestrial $\delta^{13}\text{C}$ signal recorded in the lignite is amplified by a factor of 3 relative to the marine record.
- This implies that there must have been an ecophysiological adaptation of terrestrial plants to account for the amplified isotopic fractionation.

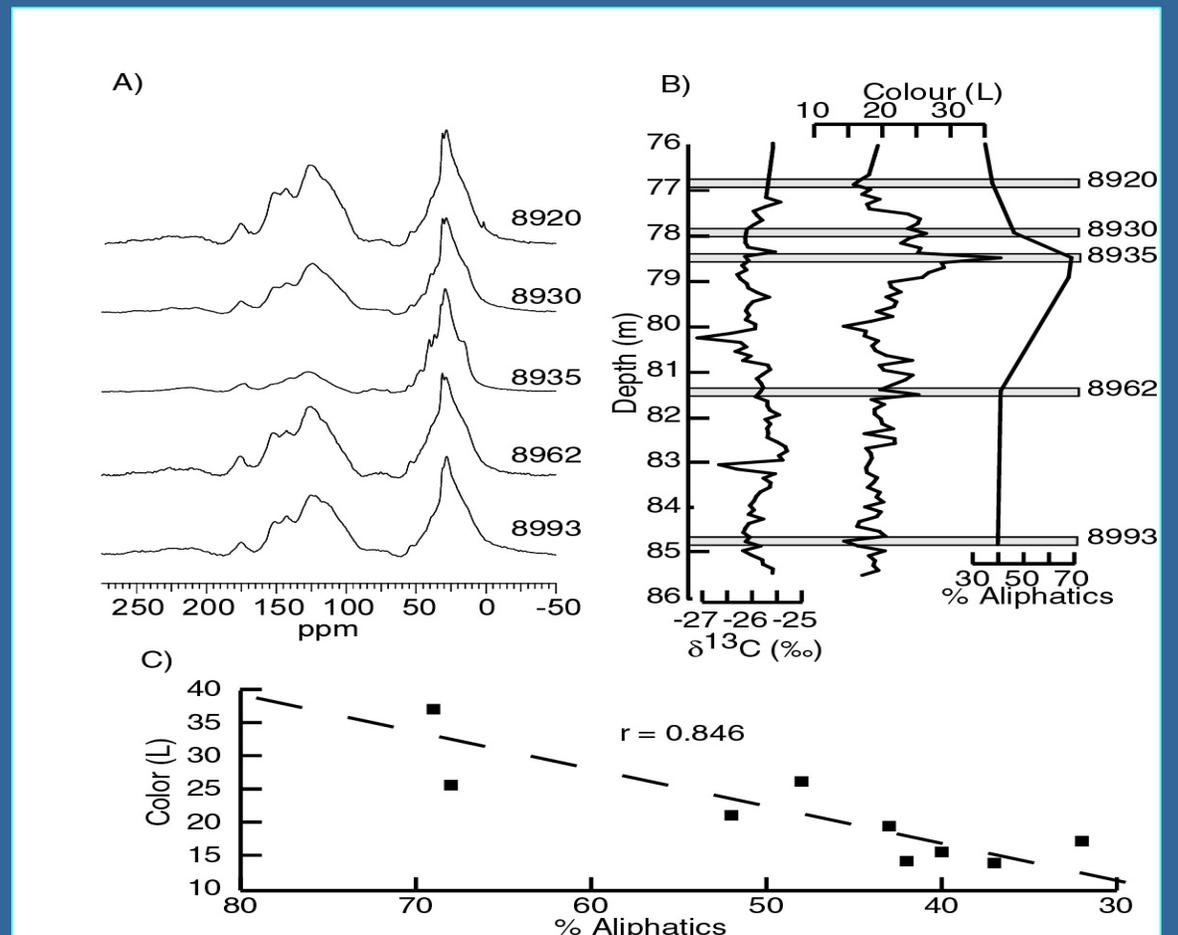


Strong correlation between brown coal colour and aliphatic carbon content

- ^{13}C NMR indicates that the proportion of aliphatic carbon correlates strongly with color ($r = 0.846$) but not with $\delta^{13}\text{C}$ ($r = -0.075$).



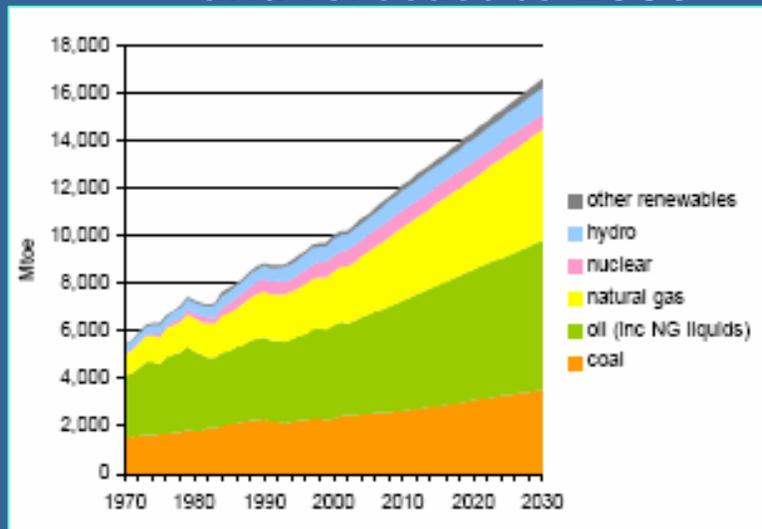
- Lignite colour is primarily a response to the conditions that govern lignin degradation in the near surface.



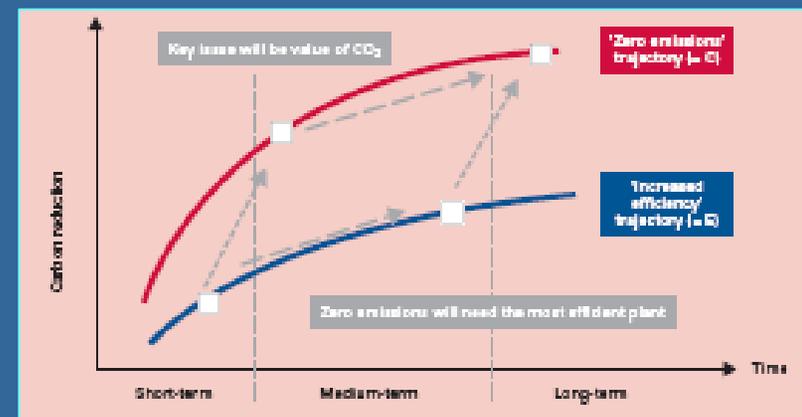
Cleaner Coal Technology

– near zero emissions

World primary energy production
(supply) by source, 1970-2002
and forecast to 2030



Pathway to near zero emissions



- Globally, coal usage is not going to decrease.
- Twin track – improved efficiency with emergence of carbon capture and storage
- Biomass co-feeding, both PF combustion and gasification.

Current and future areas of coal research

- *CCS, near zero emissions*



The University of
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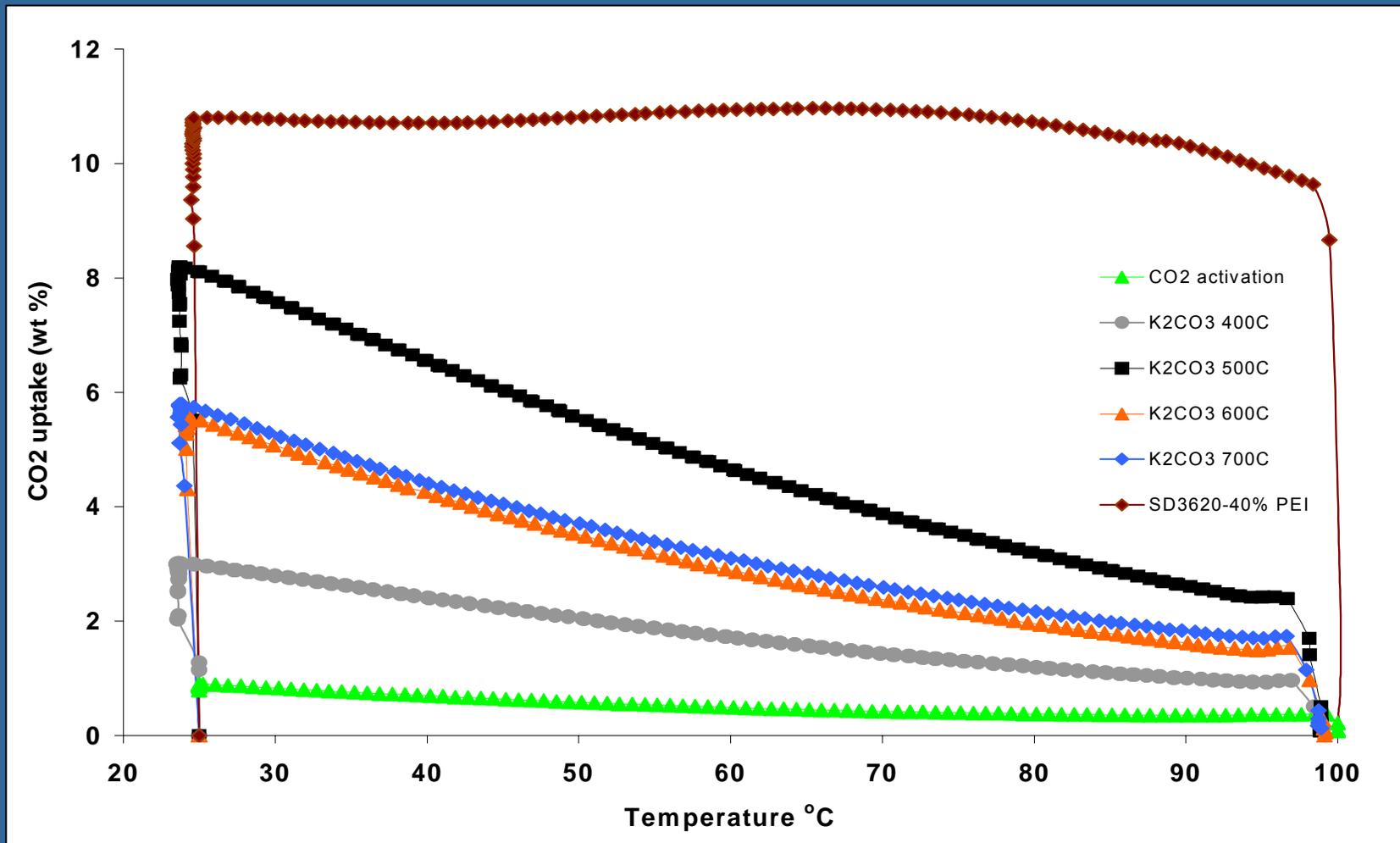
- In terms of coal structure, the emphasis on understanding combustion and gasification behaviour has focused on identifying the least reactive macerals and the influence of minerals on reactivity, as well as slagging and fouling.
- Pollutant control including CO₂ capture is key area and this draws on related disciplines such as adsorption, catalysis, membranes, trace metal associations and bonding.
- Understanding the mode of attachment of Hg and Pt (**Janos Lakatos**) has laid the foundation to pursue the development of novel adsorbents/reductants for CO₂, NO_x and Hg.
- Still a need for traditional coal science – fluidity behaviour to achieve higher coke yields (i.e. using lower volatile blends) whilst avoiding high coking pressures.

UF-resin chemical activation

- vast improvement in CO₂ adsorption, maximising at 500°C



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Preparation of nitrogen enriched carbons for CO₂ capture

MTX: Carbon matrix (sugar) infused with nitrogen source (X)

Physical mixing of sugar with nitrogen source

Hydrolysis of mixture with sulphuric acid

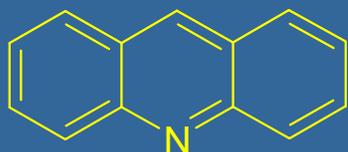
Carbonisation - 400 °C, 30 minutes

Surface area enhancement: **Activation** - physical or chemical

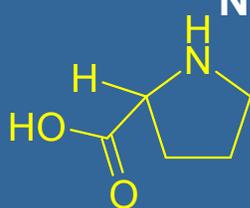
UR - Urea-formaldehyde resin

Curing: 2 Hrs 120 °C under nitrogen

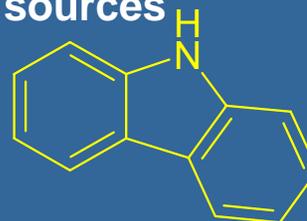
Nitrogen sources



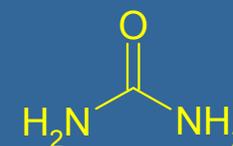
acridine **A**



proline **P**

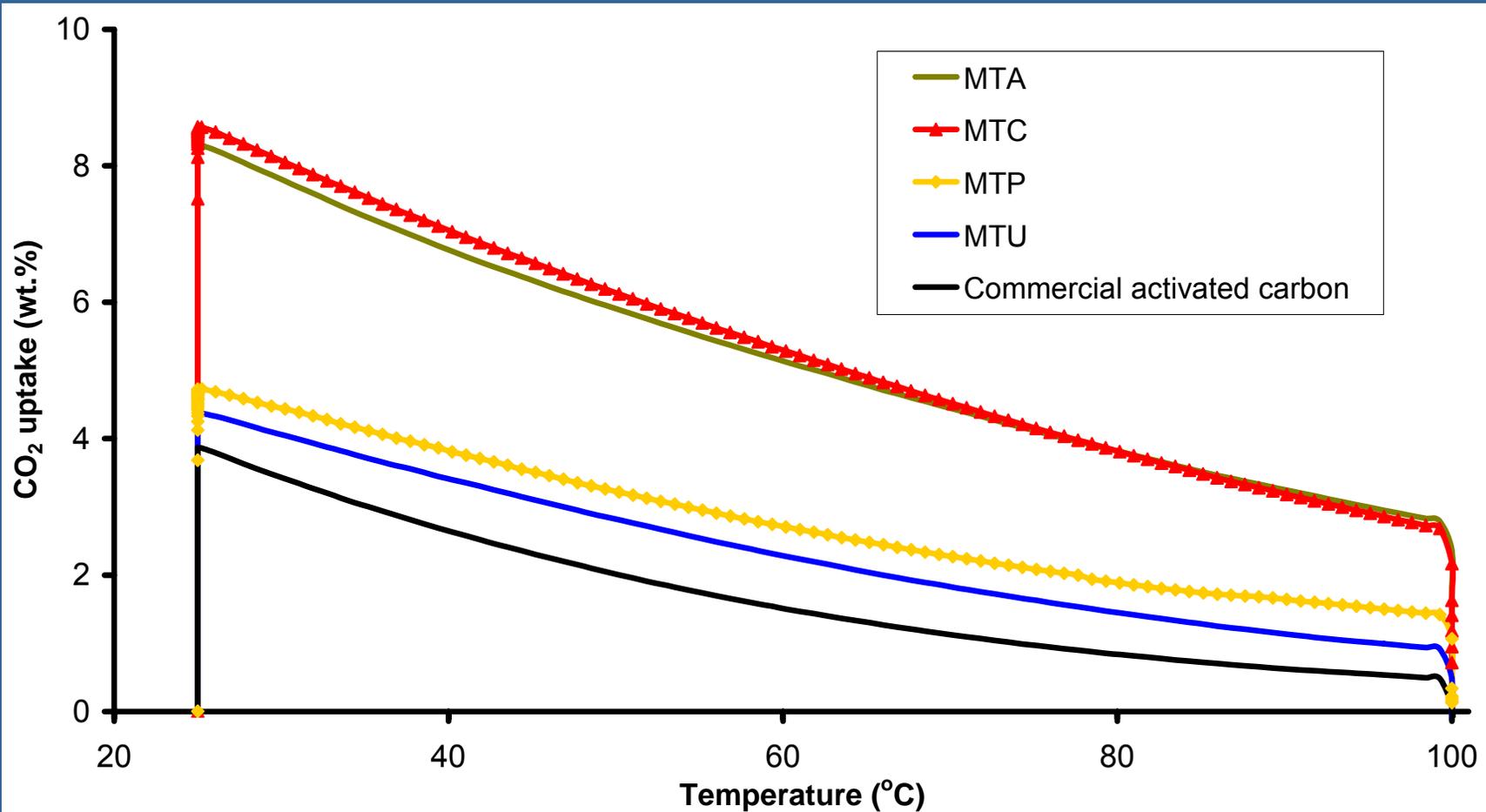


carbazole **C**



urea **U**

Influence of temperature on CO₂ uptake of co-pyrolysed sugars



Collaborators Worldwide



Spain – INCAR,
Univ. of Alicante

Chinese Acad.
of Sciences

Australia – CSIRO,
Univ. of Melbourne/
Monash

USA – Argonne, Oak
Ridge and Sandia Nat.
Labs, Penn State Univ.

Brazil, Campinas
Univ., Petrobras

ICCS&T 2007

Note in your diaries



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- **Nottingham, 28-31 August 2007**

